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De novo asymmetric bio- and chemocatalytic synthesis of saccharides stereoselective formal O-glycoside bond formation using palladium catalysis

Comely, Alex C.; Eelkema, Rienk; Minnaard, Adriaan J.; Feringa, Ben L.

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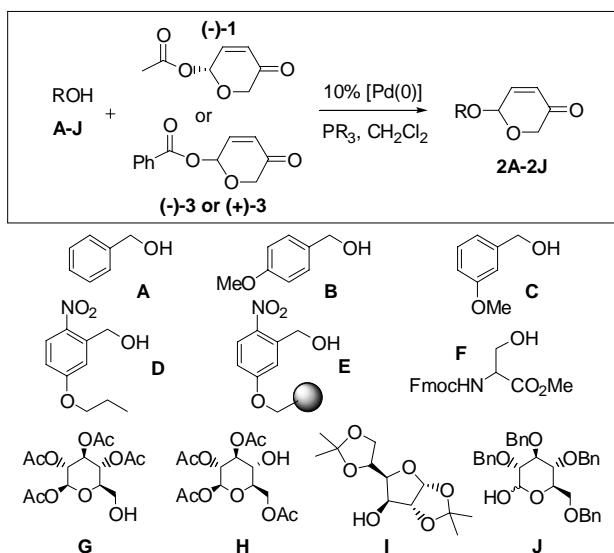
Supplementary Material

***De Novo* Asymmetric Bio- and Chemocatalytic Synthesis of Saccharides – Stereoselective Formal O-Glycoside Bond Formation Under Palladium Catalysis**

Alex C. Comely, Rienk Eelkema, Adriaan J. Minnaard and Ben L. Feringa*

Department of Organic and Molecular Inorganic Chemistry, University of Groningen, Nijenborgh 4, 9747 AG
Groningen, The Netherlands

General experimental remarks: Reagents were purchased from Aldrich, Acros Chimica, Strem, Merck or Fluka and were used as provided unless otherwise stated. All solvents were reagent grade and were dried and distilled before use according to standard procedures. Removal of ethanol, used as a stabilising agent, from dichloromethane was effected by washing with conc. H₂SO₄ (x2), water (x2), 5% Na₂SO₄ (x2), water (x2) and drying over CaCl₂ before distillation from CaH₂. Chromatography: silica gel, Merck type 9385 230-400 mesh, TLC: silica gel 60, Merck, 0.25 mm. Optical rotations were measured on a Perkin Elmer 241 MC at ambient temperature. Mass spectra (HRMS) were recorded on an AEI MS-902 by Mr. A. Kiewiet. GC analyses were performed on a HP5890 Series II using a flame ionisation detector and using the chiral columns specified in the table at the end of this section. HPLC analyses were performed on a Shimadzu 10AD-VP using the chiral columns specified in the table at the end of this section. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini-200 (50.32 MHz), Varian 300 (75.48 MHz) or Varian 500 (125.80 MHz) spectrometer in CDCl₃. Chemical shift values are denoted in δ values (ppm) relative to residual solvent peaks (CHCl₃, ¹H δ=7.26, ¹³C δ=77).



(*R*)-(-)-6-Acetoxy-2*H*-pyran-3(6*H*)-one, (-)-**1**

To a solution of (\pm)-**1** (5 g, 32 mmol, prepared according to a literature procedure) in 1,4-dioxane (300ml) was added *n*-butanol (11.9 g, 14.6 ml, 160 mmol) and Lipase PS-HSC (2.5 g, 30% loading w/w) and the resulting mixture was stirred with a mechanical over-head stirrer at ambient temperature for 48 h. The suspension was filtered through celite, eluted with DCM and concentrated to a pale yellow oil *in vacuo*. Purification by column chromatography (SiO_2 , hexane:EtOAc 7:3) gave the title compound (2.07 g, 13.2 mmol, 41%) as a colourless oil which crystallised at 4 °C. The pale yellow oily crystals were washed with ice-cold EtOAc/pentane (1:19) to afford the highly pure title compound (1.87 g, 75%, >99% ee) as colourless crystals. $[\alpha]_{\text{D}} -198^\circ$ (c 1.0, CHCl_3)

(*R*)-(-)-6-Benzoyloxy-2*H*-pyran-3(6*H*)-one, (-)-**3** and (*S*)-(+)-6-Benzoyloxy-2*H*-pyran-3(6*H*)-one, (+)-**3**

The racemate (prepared according to a literature procedure) was resolved by preparative HPLC (Chiralpac AS column, heptane/2-propanol 9:1). (*S*)-(+)-**3** (RT 8.3 min) $[\alpha]_{\text{D}} +289.8^\circ$ (c 1.370, CH_2Cl_2); (*R*)-(-)-**3** (RT 10.7 min) $[\alpha]_{\text{D}} -284.7^\circ$ (c 1.330, CH_2Cl_2).

(*R,S*)-(\pm)-6-Benzoyloxy-2*H*-pyran-3(6*H*)-one (**\pm**)-2**A** (prepared from (\pm)-6-Acetoxy-2*H*-pyran-3(6*H*)-one (**\pm**)-1)

To palladium (II) acetate (11.3 mg, 5 mol%, 0.05 mmol) in a flame-dried Schlenk tube under argon was added a solution of triphenylphosphite (34 mg, 11 mol%, 0.11 mmol) in DCM (2 ml) *via* cannula. After stirring the yellow solution at ambient temperature for 10 min, benzyl alcohol (162 mg, 155 μ l, 1.5 mmol) was added *via* microsyringe. After stirring the resulting deep brown solution for a further 10 min a solution of (\pm)-6-acetoxy-2*H*-pyran-3(6*H*)-one (**\pm**)-1 (156 mg, 1 mmol) in DCM (1 ml) was added and the mixture was stirred in the dark for 24 h. The homogeneous orange solution was preadsorbed on silica and purified by column chromatography (SiO₂, acetone:pentane) to give the title compound (153 mg, 75%) as a colourless oil. Anal. Calcd. for C₁₃H₁₄O₄: C, 70.58; H, 5.92%. Found: C, 70.55; H, 6.00. ¹H NMR (300 MHz, CDCl₃) 7.34-7.38 (m, 5 H), 6.88 (dd, 1 H, *J* = 10.26 and 3.3 Hz), 6.14 (d, 1 H, *J* = 10.26 Hz), 5.29 (d, 1 H, *J* = 3.66 Hz), 4.85 (d, 1 H, *J* = 11.72 Hz), 4.66 (d, 1 H, *J* = 11.72 Hz), 4.49 (d, 1 H, *J* = 16.84 Hz) and 4.12 (d, 1 H, *J* = 16.84 Hz). ¹³C NMR (75 MHz, CDCl₃) 194.4, 144.2, 136.8, 128.5, 128.1, 128.1, 127.8, 92.0, 70.6 and 66.2. MS (EI): *m/z* 204 (M⁺, 1%) and 91 (C₇H₇, 100). HRMS calcd. for C₁₃H₁₄O₄: 204.07863. Found: 204.07789.

(*S*)-(-)-6-Benzoyloxy-2*H*-pyran-3(6*H*)-one, (-)-2**A**

To palladium (II) acetate (22.5 mg, 10 mol%, 0.1 mmol) in a flame-dried Schlenk tube under argon was added a solution of triphenylphosphite (68 mg, 22 mol%, 0.22 mmol) in DCM (2 ml) *via* cannula. After stirring the yellow solution at ambient temperature for 10 min, benzyl alcohol (162 mg, 155 μ l, 1.5 mmol) was added *via* microsyringe. After stirring for a further 10 min the resulting mixture was cooled to -30 °C and a solution of (-)-6-acetoxy-2*H*-pyran-3(6*H*)-one (-)-1 (156 mg, 1 mmol) in DCM (1 ml), also cooled to -30 °C, was added. The mixture was stirred in the dark for 24 h at -30 °C. The homogeneous orange solution was preadsorbed on silica and purified by column chromatography (SiO₂, acetone:pentane) to give the title compound (169 mg, 83%) as a colourless oil. [α]_D = -45.5° (94% ee, c 1.09, CH₂Cl₂)

(*R,S*)-(\pm)-6-Benzoyloxy-2*H*-pyran-3(6*H*)-one, (**\pm**)-2**A** (prepared from (\pm)-6-benzoyloxy-2*H*-pyran-3(6*H*)-one (**\pm**)-3)

To palladium (II) acetate (5.2 mg, 5 mol%, 0.023 mmol) in a flame-dried Schlenk tube under argon was added a solution of triphenylphosphite (15.6 mg, 11 mol%, 0.051 mmol) in DCM (2 ml) *via* cannula. After stirring the yellow solution at ambient temperature for 10 min, benzyl alcohol (74 mg, 71 μ l, 0.69 mmol) was added *via* microsyringe. After stirring the resulting deep brown solution for a further 10 min a solution of (\pm)-6-benzoyloxy-2*H*-pyran-3(6*H*)-one (**\pm**)-3 (100 mg, 0.46 mmol) in DCM (1 ml) was added and the mixture was stirred in the dark for 24 h. The homogeneous orange solution

was preadsorbed on silica and purified by column chromatography (SiO₂, acetone:pentane 5:95) to give the title compound (82 mg, 87%) as a colourless oil.

(R,S)-(±)-6-(4-Methoxybenzyl)oxy-2*H*-pyran-3(6*H*)-one, (±)-**2B**

Prepared according to the procedure for (±)-**2A** from palladium(II) acetate (15 mg, 5 mol%, 0.07 mmol), triphenylphosphite (45 mg, 11 mol%, 0.15 mmol), 4-methoxybenzyl alcohol (184 mg, 1.3 mmol) and (±)-6-acetoxy-2*H*-pyran-3(6*H*)-one **1** (250 mg, 1.6 mmol) in DCM (6 ml). Purification of the residue by column chromatography (SiO₂, EtOAc:hexane 5:95 to 15:85 gradient elution) and distillation of remaining (±)-**1** from the mixture (120 °C, 1 mmHg) gave product (±)-**2B** (mg, 1.27 mmol, 79%) as a colourless oil. Anal. Calcd. for C₁₃H₁₄O₄: C, 66.66; H, 6.02%. Found: C, 66.66; H 6.07. ¹H NMR (300 MHz, CDCl₃) 7.22 (d, 2 H, *J* = 8.79 Hz), 6.82 (d, 2 H, *J* = 8.42 Hz), 6.79 (dd, 1 H, *J* = 3.29 and 6.96 Hz), 6.05 (d, 1 H, *J* = 10.62 Hz), 5.19 (d, 1 H, *J* = 3.29 Hz), 4.71 (d, 1 H, *J* = 11.35 Hz), 4.52 (d, 1 H, *J* = 11.35 Hz), 4.40 (d, 1 H, *J* = 16.85 Hz), 4.04 (d, 1 H, *J* = 16.84 Hz) and 3.73 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃) 194.6, 159.5, 144.4, 129.8, 128.8, 127.8, 113.9, 91.7, 70.3, 66.2 and 55.2. MS (EI): *m/z* 234 (M⁺, 23%) and 121 (CH₃OC₆H₄CH₂, 100). HRMS calcd. for C₁₃H₁₄O₄: 234.08919. Found: 234.08864.

(S)-(-)-6-(4-Methoxybenzyl)oxy-2*H*-pyran-3(6*H*)-one, (-)-**2B**

Prepared according to the procedure for (-)-**2A** from palladium(II) acetate (7.2 mg, 10 mol%, 0.032 mmol), triphenylphosphite (22 mg, 22 mol%, 0.071 mmol), 4-methoxybenzyl alcohol (44 mg, 0.32 mmol) and (-)-6-acetoxy-2*H*-pyran-3(6*H*)-one **1** (100 mg, 0.64 mmol) in DCM (3 ml). Purification of the residue (98% ee, HPLC) as described for (±)-**2B** gave (-)-**2B** (65 mg, 87%, 74% ee) as a colourless oil.

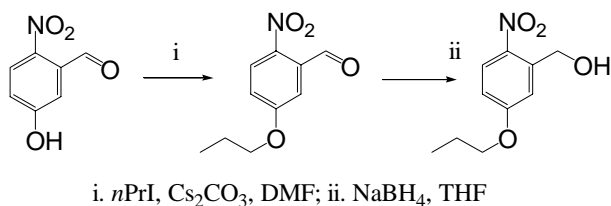
(R,S)-(±)-6-(3-Methoxybenzyl)oxy-2*H*-pyran-3(6*H*)-one, (±)-**2C**

Prepared according to the procedure for (±)-**2A** from palladium (II) acetate (60 mg, 5 mol%, 0.27 mmol), triphenylphosphite (182 mg, 11 mol%, 0.59 mmol), 3-methoxybenzyl alcohol (736 mg, 5.3 mmol) and (±)-6-acetoxy-2*H*-pyran-3(6*H*)-one (±)-**1** (1.25 g, 8 mmol) in DCM (24 ml). Purification of the residue by column chromatography (SiO₂, acetone:pentane 1:9) gave product (±)-**2C** (1.122 g, 90%) as a colourless oil. Anal. Calcd. for C₁₃H₁₄O₄: C, 66.66; H, 6.02%. Found: C, 66.52; H, 6.01. ¹H NMR (300 MHz, CDCl₃) 7.23-7.29 (m, 1 H), 6.82-6.93 (m, 3 H), 6.12 (d, 1 H, *J* = 10.6 Hz), 5.6 (d, 1 H, *J* = 3.29 Hz), 4.80 (d, 1 H, *J* = 11.7 Hz), 4.61 (d, 1 H, *J* = 11.7 Hz), 4.47 (d, 1 H, *J* = 16.8 Hz), 4.09

(d, 1 H, $J = 16.8$ Hz) and 3.78 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3) 194.5, 159.7, 144.2, 138.3, 129.5, 129.4, 127.8, 120.2, 113.48, 113.45, 91.9, 70.4, 66.2 and 55.1. MS (EI): m/z 234 (M^+ , 8%) and 122 ($\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_3$, 100). HRMS calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_4$: 234.08919. Found: 234.09062.

(*S*)-(-)-6-(3-Methoxybenzyl)oxy-2*H*-pyran-3(6*H*)-one, (-)-**2C**

Prepared according to the procedure for (-)-**2A** from palladium (II) acetate (45 mg, 10 mol%, 0.2 mmol), triphenylphosphite (136 mg, 22 mol%, 0.44 mmol), 3-methoxybenzyl alcohol (276 mg, 2 mmol) and (-)-6-acetoxy-2*H*-pyran-3(6*H*)-one (-)-**1** (468 mg, 3 mmol) in DCM (6 ml). Purification of the residue as described for (\pm)-**2C** gave (-)-**2C** (460 mg, 98%, 99% ee) as a colourless oil. $[\alpha]_{\text{D}} = -36.2^\circ$ (99% ee, c 1.4, CH_2Cl_2)



2-Nitro-5-*n*-propoxybenzaldehyde

To a solution of iodopropane (10.2 g, 5.9 ml, 0.6 mmol) in DMF (100 ml) at ambient temperature was added Cs_2CO_3 (9.8 g, 0.3 mmol) and 5-hydroxy-2-nitrobenzaldehyde (5 g, 0.3 mmol) and the resulting mixture was stirred for 36 h. After diluting with water (50 ml) and extraction with EtOAc (3 x 50 ml) the organic layers were dried with MgSO_4 and concentrated to an orange oil. Trituration with hexane (50 ml) gave a pale brown precipitate which was filtered and dried *in vacuo* to give 2-nitro-5-*n*-propoxybenzaldehyde (4.92 g, 79%) as a pale brown solid which was not purified further. Anal. Calcd. for $\text{C}_{10}\text{H}_{11}\text{NO}_4$: C, 57.41; H, 5.30; N, 6.70%. Found: C, 57.36; H, 5.35; N, 6.69. ^1H NMR (300 Mz, CDCl_3) 10.47 (s, 1 H), 8.14 (d, 1 H, $J = 9.15$ Hz), 7.30 (d, 1 H, $J = 2.93$ Hz), 7.13 (dd, 1 H, $J = 8.79$ and 2.56 Hz), 4.06 (t, 2 H, $J = 6.23$ Hz), 1.86 (m, 2 H), 1.05 (t, 3 H, $J = 7.32$ Hz). ^{13}C NMR (75 Mz, CDCl_3) 188.61, 163.64, 141.97, 127.22, 118.84, 113.68, 70.78, 22.21, 10.30. MS (EI): m/z 209 (M^+ , 5%), 167 ($\text{M} - \text{C}_3\text{H}_6$, 100). HRMS calcd. for $\text{C}_{10}\text{H}_{11}\text{NO}_4$: 209.06878. Found: 209.06983.

2-Nitro-5-*n*-propoxybenzyl alcohol

To a solution of 2-nitro-5-*n*-propoxybenzaldehyde (4.5 g, 21.5 mmol) in THF (45 ml) at 0 °C was added NaBH₄ (818 mg, 21.5 mmol) and ethanol (1 ml). After stirring for 30 min at 0 °C and 30 min at ambient temperature the mixture was cooled again to 0 °C, quenched with satd. NH₄Cl (50 ml) and extracted with EtOAc (3 x 50 ml). The organic layers were washed with brine and dried over MgSO₄ to give a pale yellow solid (4.5 g, quant) which was not purified further. Anal. Calcd. for C₁₀H₁₁NO₄: C, 56.87; H, 6.20; N, 6.63%. Found: C, 56.68; H, 6.24; N, 6.56. ¹H NMR (200 MHz, CDCl₃) 8.14 (d, 1 H, *J* = 9.28 Hz), 7.19 (d, 1 H, *J* = 2.68 Hz), 6.85 (dd, 1 H, *J* = 9.28 and 2.93 Hz), 4.96 (s, 2 H), 4.02 (t, 2 H, *J* = 6.35 Hz), 2.77 (brs, 1 H), 1.83 (sextet, 2 H, *J* = 7.57 Hz), 1.04 (t, 3H, *J* = 7.32 Hz). ¹³C NMR (50 MHz, CDCl₃) 163.83, 140.2, 139.90, 127.93, 114.47, 113.41, 70.26, 62.87, 22.27, 10.33. MS (EI): *m/z* 211 (M⁺, 62%), 194 (M – OH, 17) and 43 (C₃H₇, 100). HRMS calcd. for C₁₀H₁₃NO₄: 211.08443. Found: 211.08535.

(*R,S*)-(±)-6-(2-Nitro-5-*n*-propoxybenzyl)oxy-2*H*-pyran-3(6*H*)-one, (±)-2D

Prepared according to the procedure for (±)-2A from palladium (II) acetate (11 mg, 5 mol%, 0.047 mmol), triphenylphosphite (32 mg, 11 mol%, 0.104 mmol), 2-nitro-5-*n*-propoxybenzyl alcohol (200 mg, 0.95 mmol) and (±)-6-acetoxy-2*H*-pyran-3(6*H*)-one (±)-1 (222 mg, 1.42 mmol) in DCM (4 ml). Purification of the residue by column chromatography (SiO₂, acetone:pentane 1:9 to 1:4 gradient elution) gave product (±)-2D (230 mg, 79%) as a colourless waxy solid. Anal. Calcd. for C₁₅H₁₇NO₆: C, 58.63; H, 5.58; N, 4.56%. Found: C, 58.75; H, 5.51; N, 4.61. ¹H NMR (300 MHz, CDCl₃) 8.19 (d, 1 H, *J* = 9.16 Hz), 7.21 (d, 1 H, *J* = 2.56 Hz), 6.99 (dd, 1 H, *J* = 3.30 and 10.25 Hz), 6.88 (dd, 1 H, *J* = 2.93 and 9.16 Hz), 6.21 (d, 1 H, *J* = 10.62 Hz), 5.41 (d, 1 H, *J* = 3.29 Hz), 5.27 (d, 1 H, *J* = 15.01 Hz), 5.10 (d, 1 H, *J* = 15.02 Hz), 4.48 (d, 1 H, *J* = 16.84 Hz), 4.16 (d, 1 H, *J* = 16.84 Hz), 4.01 (t, 2 H, *J* = 6.6 Hz), 1.85 (sextet, 2 H, *J* = 7.32 Hz) and 1.06 (t, 3 H, *J* = 7.32 Hz). ¹³C NMR (75 MHz, CDCl₃) 194.2, 163.5, 143.7, 139.6, 136.8, 128.0, 127.7, 114.0, 112.6, 93.1, 70.1, 67.9, 66.3, 22.2 and 10.3. MS (EI): *m/z* 307 (M⁺, 3%), 210 (M – C₅H₅O₂, 27), 194 (M – C₅H₅O₃, 100) and 178 (M – C₅H₅O₄, 34). HRMS calcd. for C₁₅H₁₇NO₆: 307.10555. Found: 307.10469.

(*S*)-(-)-6-(2-Nitro-5-*n*-propoxybenzyl)oxy-2*H*-pyran-3(6*H*)-one, (-)-2D

Prepared according to the procedure for (-)-2A from palladium (II) acetate (34 mg, 10 mol%, 0.15 mmol), triphenylphosphite (102 mg, 22 mol%, 0.33 mmol), 2-nitro-5-*n*-propoxybenzyl alcohol (317 mg, 1.5 mmol) and (-)-6-acetoxy-2*H*-pyran-3(6*H*)-one (-)-1 (468 mg, 3 mmol) in DCM (9 ml). Purification of the residue as described for (±)-2D gave (-)-2D (388 mg, 84%, >98% ee) as a colourless waxy solid. [α]_D = -94.9° (98% ee, c 0.78, CH₂Cl₂)

Phenolic polystyrene-supported 2-Nitro-5-*n*-propoxybenzyl alcohol, **E**

Spectra included: ^{13}C NMR

To a suspension of phenolic polystyrene (500 mg, 1.45 mmol[O] g^{-1} , 0.725 mmol, 1% DVB) in DMF (10 ml) was added Cs_2CO_3 (473 mg, 1.45 mmol) and 5-(3-iodopropoxy)-2-nitrobenzyl alcohol (489 mg, 1.45 mmol). After shaking at ambient temperature for 60 h the resin was filtered and washed with THF/ H_2O (1:1 at 0 °C rapidly, 0:1 at RT, 1:1, 3:1 and 9:1; 2 x 20ml each), THF (2 x 2 ml) and CH_2Cl_2 (2 x 2ml). The resulting yellow residue was dried *in vacuo* for 24 h to give resin **E** (582 mg, 54%, 0.67 mmol[linker] g^{-1}). ^{13}C -NMR (75 MHz, CDCl_3 -swollen resin) diagnostic signals 163.0 ($\text{C}_{\text{ar}}\text{-O}$), 113.3 and 112.8 (2 x $\text{C}_{\text{ar}}\text{-H}$), 65.3 (2 x $\text{C}_{\text{ar}}\text{-O-CH}_2$), 62.7 ($\text{C}_{\text{ar}}\text{-CH}_2$) and 29.0 ($\text{CH}_2\text{-CH}_2\text{-CH}_2$). ν_{max} cm^{-1} 1511 (asymm/symm N=O), 1322 (C- NO_2).

Phenolic polystyrene-supported-(*R,S*)-6-(2-Nitro-5-*n*-propoxybenzyl)oxy-2*H*-pyran-3(6*H*)-one, **2E**

Spectra included: ^{13}C NMR

To a suspension of resin **E** (200 mg, 0.134 mmol) in CH_2Cl_2 (1 ml) under Ar was added a solution of $\text{Pd}(\text{OAc})_2$ (3 mg, 0.0134 mmol) and triphenylphosphite (9 mg, 0.0295 mmol) in CH_2Cl_2 (0.5 ml) *via* cannula. The resulting mixture was shaken for 10 min before addition of a solution of 6-acetoxy-2*H*-pyran-3(6*H*)-one (**±**)-**1** (42 mg, 0.268 mmol) in CH_2Cl_2 (0.5 ml) *via* cannula. After shaking for 24 h, the resin was filtered and washed with CH_2Cl_2 (2 x 2 ml), THF/ H_2O (1:1, 3:1 and 9:1; 2 x 2ml each), THF (2 x 2 ml) and CH_2Cl_2 (2 x 2ml). The resulting black residue was dried *in vacuo* to give **2E** (209 mg, 69%). ^{13}C -NMR (50.3 MHz, CDCl_3 -swollen resin) diagnostic signals 194.1 (C=O), 163.3 ($\text{C}_{\text{ar}}\text{-O}$), 143.6 (CH=CH-C=O), 113.3 and 112.6 (2 x $\text{C}_{\text{ar}}\text{-H}$), 93.2 (CH-O), 68.0 and 65.3 (2 x $\text{C}_{\text{ar}}\text{-O-CH}_2$), 66.5 ($\text{CH}_2\text{-C=O}$), 62.6 ($\text{C}_{\text{ar}}\text{-CH}_2$) and 28.9 ($\text{CH}_2\text{-CH}_2\text{-CH}_2$). ν_{max} cm^{-1} 1703 (s, C=O), 1512 (asymm/symm N=O), 1323 (C- NO_2).

6(*R,S*)-(Fmoc-Ser-OMe)-2*H*-pyran-3(6*H*)-one, **6(R,S)-2F**

Prepared according to the procedure for (**±**)-**2A** from palladium (II) acetate (3.3 mg, 5 mol%, 0.015 mmol), triphenylphosphite (10 mg, 11 mol%, 0.032 mmol), Fmoc-Ser-OMe (100 mg, 0.29 mmol) and (**±**)-6-acetoxy-2*H*-pyran-3(6*H*)-one (**±**)-**1** (69 mg, 0.44 mmol) in DCM (3 ml). Purification of the residue by column chromatography (SiO_2 , EtOAc/pentane 1:4 to 3:7 gradient elution) gave product **6(R,S)-2F** (35 mg, 27%) as a mixture of 2 diastereomers (1:1) as a colourless solid foam. Anal. Calcd. for $\text{C}_{24}\text{H}_{23}\text{NO}_7$: C, 65.90; H, 5.30; N, 3.20%. Found: C, 65.6; H, 5.5; N, 2.9.

^1H NMR (300 MHz, CDCl_3) 7.77 (d, 2 H, $J = 7.32$ Hz), 7.62-7.60 (m, 2 H), 7.44-7.30 (m, 4 H), 6.87-6.79 (m, 1 H), 6.14 (d, 1 H, $J = 10.26$ Hz), 5.75-5.62 (m, 1 H), 5.18 (brs, 1 H), 4.62-4.58 (m, 1 H), 4.51-4.06 (m, 6 H) and 3.89-3.71 (m, 4 H). ^{13}C NMR (75 MHz, CDCl_3) 194.1, 193.9, 170.3, 170.1, 155.8, 143.7, 143.6, 143.4, 141.2, 128.0, 128.0, 127.7, 127.0, 125.0, 119.9, 93.6, 93.1, 69.4, 68.7, 67.1, 67.0, 66.4, 66.1, 54.2, 54.0, 52.7, 47.0 and 47.0. MS (EI): m/z 437 (M^+ , 1%), 378 ($\text{M} - \text{CO}_2\text{CH}_3$, 1) and 178 ($\text{C}_{14}\text{H}_{10}$, 100). HRMS calcd. for $\text{C}_{15}\text{H}_{17}\text{NO}_6$: 437.14745. Found: 437.14655.

6(*S*)-(Fmoc-Ser-OMe)-2*H*-pyran-3(6*H*)-one, **6(*S*)-2F**

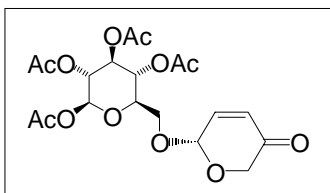
Prepared according to the procedure for (-)-**2A** from palladium (II) acetate (4.5 mg, 10 mol%, 0.02 mmol), triphenylphosphite (14 mg, 22 mol%, 0.044 mmol), Fmoc-Ser-OMe (68 mg, 0.2 mmol) and (-)-6-acetoxy-2*H*-pyran-3(6*H*)-one (-)-**1** (47 mg, 0.3 mmol) in DCM (1.5 ml). Purification of the residue as described for **6(*R,S*)-2F** gave **6(*S*)-2F** (68 mg, 78%, 97% ee) as a colourless solid foam. ^1H NMR (300 MHz, CDCl_3) 7.77 (d, 2 H, $J = 7.7$ Hz), 7.59-7.58 (m, 2 H), 7.43-7.29 (m, 4 H), 6.81 (dd, 1 H, $J = 10.3$ and 2.9 Hz), 6.14 (d, 1 H, $J = 10.25$ Hz), 5.77 (d, 1 H, $J = 8.42$ Hz), 5.18 (brs, 1 H), 4.61-4.58 (m, 1 H), 4.45-4.37 (m, 3 H), 4.24 (t, 1 H, $J = 7.0$ Hz), 4.13-4.07 (m, 3 H) and 3.78 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3) 193.9, 170.3, 155.9, 143.7, 143.6, 143.3, 141.3, 128.1, 127.7, 127.0, 125.0, 124.9, 120.0, 93.7, 69.5, 67.2, 66.4, 54.2, 52.7 and 47.0. $[\alpha]_{\text{D}} = -22.2^\circ$ (97% ee, c 1.80, CH_2Cl_2).

6(*R,S*)-*O*-(6-oxo-2*H*-pyran-3(6*H*)-one)-1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranoside, **6(*R,S*)-2G**

Prepared according to the procedure for (\pm)-**2A** from palladium (II) acetate (11.3 mg, 10 mol%, 0.05 mmol), triphenylphosphite (34 mg, 22 mol%, 0.11 mmol), 1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose (174 mg, 0.5 mmol) and (\pm)-6-acetoxy-2*H*-pyran-3(6*H*)-one (\pm)-**1** (156 mg, 1.0 mmol) in DCM (2 ml). Purification of the residue by column chromatography (SiO_2 , EtOAc/pentane 2:3) gave 2 diastereomers (ratio 0.45:0.55) of product **6(*R,S*)-2G** (191 mg, 86%) as a colourless foam. ^1H NMR (300 MHz, CDCl_3): δ 6.89 (dd, $J = 8.79, 3.30$ Hz, 0.55 *H*, diastereomer), 6.86 (dd, $J = 10.25, 3.66$ Hz, 0.45 *H*, diastereomer), 6.12 (d, $J = 10.25$ Hz, 1 H), 5.69 (d, $J = 7.33, 0.45$ H), 5.67 (d, $J = 6.95, 0.55$ H), 5.29-5.07 (m, 4 H), 4.45 (d, $J = 16.11$ Hz, 0.55 *H*), 4.39 (d, $J = 16.84$ Hz, 0.45 *H*), 4.06 (d, $J = 17.95$ Hz, 0.55 *H*), 4.02 (d, $J = 16.48$ Hz, 0.45 *H*), 3.88-3.61 (m, 3H), and 2.05 (m, 12 H). ^{13}C NMR (75 MHz, CDCl_3): 194.3, 194.2, 170.0, 169.9, 169.4, 169.2, 169.1, 169.1, 168.9, 168.8, 143.7, 143.4, 127.8, 127.1, 93.9, 93.0, 91.6, 91.6, 74.0, 73.3, 72.8, 72.7, 70.1, 70.0, 68.3, 68.2, 67.1, 66.4, 66.10, 66.05, 20.6, 20.5 and 20.4.

6(*S*)-*O*-(6-oxo-2*H*-pyran-3(6*H*)-one)-1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranoside, **6(*S*)-2G**

Spectra included: ^1H and ^{13}C NMR



(From (-)-6-Acetoxy-2*H*-pyran-3(6*H*)-one (-)-**1**)

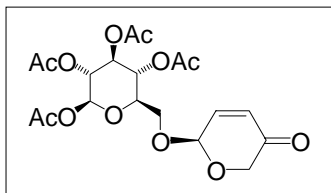
Prepared according to the procedure for (-)-**2A** from palladium (II) acetate (5.6 mg, 10 mol%, 0.025 mmol), triphenylphosphite (17.1 mg, 22 mol%, 0.055 mmol), 1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose (87 mg, 0.25 mmol) and (-)-6-acetoxy-2*H*-pyran-3(6*H*)-one (-)-**1** (59 mg, 0.375 mmol) in DCM (1 ml) at -5°C . Purification of the residue (94% de, ^1H NMR) by flash chromatography (SiO_2 , 20-50% EtOAc/pentane gradient elution) gave the product **6(*S*)-2G** (86 mg, 77%) as a colourless foam. $[\alpha]_{\text{D}} = -14.8^\circ$ (c 1.76, CH_2Cl_2). ^1H NMR (300 MHz, CDCl_3): 6.87 (dd, $J = 10.25$ and 3.29 Hz, 1H), 6.13 (d, $J = 10.26$ Hz, 1 H), 5.70 (d, $J = 8.06$ Hz, 1 H), 5.28-5.09 (m, 4 H), 4.40 (d, $J = 16.84$ Hz, 1 H), 4.03 (d, $J = 16.85$ Hz, 1 H), 3.90-3.75 (m, 3 H), 2.10 (s, 3 H), 2.03 (s, 6 H) and 2.01 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3): 194.2, 170.1, 169.3, 169.2, 168.9, 143.4, 127.9, 93.1, 91.7, 73.4, 72.9, 70.1, 68.4, 66.5, 66.2, 20.7, 20.6, 20.5 and 20.5. MS (CI) for $\text{C}_{19}\text{H}_{24}\text{O}_{12}$: m/z 462 ($\text{M}+\text{NH}_4^+$, 100%). HRMS ($\text{M}-\text{CH}_2\text{O}$) calcd. for $\text{C}_{18}\text{H}_{22}\text{O}_{11}$: 414.11615. Found: 414.11651.

(From (-)-6-Benzoyloxy-2*H*-pyran-3(6*H*)-one, (-)-**3**)

To $\text{Pd}_2(\text{dba})_3$ (1.4 mg, 5 mol%, 1.5 μmol) and), triphenylphosphine (1.8 mg, 22 mol%, 6.7 μmol) and molecular sieves (4 Å) in a flame-dried Schlenk tube under argon was added DCM (1 ml). After stirring the resulting yellow solution at ambient temperature for 10 min, 1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose (11 mg, 0.031 mmol) was added as a solid. After a further 10 min stirring and cooling of the mixture to -10°C , (-)-6-benzoyloxy-2*H*-pyran-3(6*H*)-one (-)-**3** (10 mg, 0.046 mmol) was added as a solid and the mixture was stirred in the dark. After 16 h, purification of the residue (94% de, ^1H NMR) by flash chromatography (SiO_2 , EtOAc/hexane 3:7 to 3.5:6.5 gradient elution) gave product **6(*S*)-2G** (12 mg, 88%) as a colourless oil.

6(*R*)-(+)-*O*-(6-oxo-2*H*-pyran-3(6*H*)-one)-1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranoside, **6(*R*)-2G**

Spectra included: ^1H and ^{13}C NMR



(From (+)-6-Benzoyloxy-2*H*-pyran-3(6*H*)-one, (+)-**3**)

Prepared according to the procedure for **6(*S*)-2G** from $\text{Pd}_2(\text{dba})_3$ (1.4 mg, 5 mol%, 1.5 μmol), triphenylphosphine (1.8 mg, 22 mol%, 6.7 μmol), 1,2,3,4-tetra-*O*-acetyl- β -D-glucopyranose (11 mg, 0.031 mmol) and (+)-6-benzoyloxy-2*H*-pyran-3(6*H*)-one (+)-**3** (10 mg, 0.046 mmol) in DCM (1 ml) under Ar at -10°C . After 16 h, purification of the residue (98% de by ^1H NMR) by flash column chromatography (SiO_2 , EtOAc/hexane 3:7 to 3.5:6.5 gradient elution) gave product **6(*R*)-2G** (13 mg, 96%) as a colourless oil. $[\alpha]_{\text{D}} = +36.7^\circ$ (c 0.6, CH_2Cl_2). ^1H NMR (300 MHz, CDCl_3): 6.90 (dd, $J = 10.62$ and 3.67 Hz, 1H), 6.13 (d, $J = 10.25$ Hz, 1H), 5.68 (d, $J = 8.42$ Hz, 1H), 5.26 (dd, $J = 9.52$ and 9.52 Hz, 1H), 5.15-5.08 (m, 3H), 4.46 (d, $J = 16.85$ Hz, 1H), 4.07 (d, $J = 16.84$ Hz, 1H), 3.91 (dd, $J = 11.71$ and 2.20 Hz, 1H), 3.86-3.80 (m, 1H), 3.64 (dd, $J = 11.72$ and 5.12 Hz, 1H), 2.10 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H) and 2.01 (s, 3H). ^{13}C NMR (75 MHz, CDCl_3): 194.4, 170.1, 169.5, 169.2, 169.0, 143.7, 127.9, 94.0, 91.7, 74.1, 72.9, 70.2, 68.3, 67.2, 66.2, 20.8, 20.6, 20.5 and 20.5. MS (CI) for $\text{C}_{19}\text{H}_{24}\text{O}_{12}$: m/z 462 ($\text{M} + \text{NH}_4$) $^+$, 100%).

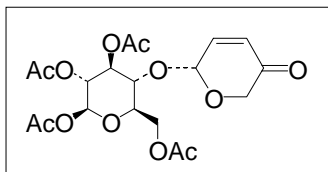
4-*O*-(6(*R,S*)-oxo-2*H*-pyran-3(6*H*)-one)-1,2,3,6-tetra-*O*-acetyl- β -D-glucopyranoside, **6(*R,S*)-2H**

Prepared according to the procedure for **6(*S*)-2G** from $\text{Pd}_2(\text{dba})_3$ (29 mg, 5 mol%, 0.025 mmol), triphenylphosphite (34 mg, 22 mol%, 0.11 mmol), 1,2,3,6-tetra-*O*-acetyl- β -D-glucopyranose (174 mg, 0.5 mmol) and (\pm)-6-acetoxy-2*H*-pyran-3(6*H*)-one (\pm)-**1** (156 mg, 1.0 mmol) in DCM (6 ml) with under Ar at ambient temperature. After 16 h, purification of the residue by column chromatography (SiO_2 , EtOAc/hexane 3:7 to 1:1 gradient elution) gave product **6(*R,S*)-2H** (130 mg, 59%) as a mixture of diastereomers (6:4) as a colourless glassy solid. ^1H NMR (300 MHz, CDCl_3): δ 6.81 (dd, $J = 10.25$ and 3.29 Hz, 0.6 H diastereomer), 6.62 (dd, $J = 10.62$ and 3.30 Hz, 0.4 H diastereomer), 6.10 (d, $J = 10.25$ Hz, 0.4 H diastereomer), 6.08 (d, $J = 10.25$ Hz, 0.6 H diastereomer), 5.69 (d, $J = 8.42$ Hz, 1H), 5.33 (d, $J = 3.29$ Hz, 0.4 H diastereomer), 5.34-5.00 (m, 2H), 5.11 (d, $J = 3.30$ Hz, 0.6 H diastereomer), 4.44-4.22 (m, 3H), 4.06-3.72 (m, 3H) and 2.11-2.00 (m, 12H). ^{13}C NMR (75 MHz, CDCl_3): 193.5, 193.1, 170.5, 170.3, 170.0, 169.5, 169.3, 169.3, 168.72, 168.67,

142.8, 142.7, 128.0, 127.4, 95.0, 94.6, 91.3, 91.3, 76.9, 74.9, 74.4, 73.4, 73.4, 73.1, 70.5, 70.4, 66.7, 66.5, 62.1, 61.5, 20.64, 20.64, 20.61, 20.61, 20.58, 20.5, 20.4 and 20.4. MS (CI) for C₁₉H₂₄O₁₂: m/z 462 (M + NH₄)⁺.

4-*O*-(6(*R*)-oxo-2*H*-pyran-3(6*H*)-one)-1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranoside, **6(*R*)-2H**

Spectra included: ¹H and ¹³C NMR



(From (-)-6-Acetoxy-2*H*-pyran-3(6*H*)-one (-)-**1**)

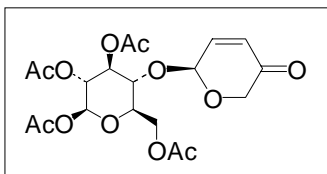
Prepared according to the procedure for 6(*S*)-(-)-**2G** from Pd₂(dba)₃ (4.6 mg, 5 mol%, 0.005 mmol), triphenylphosphine (5.8 mg, 22 mol%, 0.022 mmol), 1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranose (35 mg, 0.1 mmol) and (-)-6-acetoxy-2*H*-pyran-3(6*H*)-one (-)-**1** (23 mg, 0.15 mmol) in DCM (2 ml) under Ar at -10 °C. After 16 h, purification of the residue (91% de, ¹H NMR) by flash column chromatography (SiO₂, EtOAc/hexane 3:7 to 1:1 gradient elution) gave product **6(*R*)-2H** (29 mg, 65%) as a colourless oil. Anal. Calcd. for C₁₉H₂₄O₁₂: requires: C, 51.35; H, 5.44%. Found: C, 51.5; H, 5.6. [α]_D = -32.6 (c 0.95, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃): δ 6.62 (dd, *J* = 10.26 and 3.3 Hz, 1H), 6.12 (d, *J* = 10.62 Hz, 1H), 5.70 (d, *J* = 8.42 Hz, 1H), 5.34 (d, *J* = 2.93 Hz, 1H), 5.28 (dd, *J* = 9.16 and 9.16 Hz, 1H), 5.05 (dd, *J* = 9.52 and 8.05 Hz, 1H), 4.37-4.25 (m, 3H), 4.08-3.98 (m, 2H), 3.79-3.73 (m, 1H), 2.10 (s, 6H), 2.09 (s, 3H) and 2.02 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz): 193.2, 170.5, 169.6, 169.5, 168.8, 142.7, 128.2, 94.8, 91.4, 75.1, 74.5, 73.3, 70.5, 66.8, 62.2, 20.72, 20.70, 20.65 and 20.5. MS (CI) for C₁₉H₂₄O₁₂: m/z 462 (M + NH₄)⁺.

(From (-)-6-benzoyloxy-2*H*-pyran-3(6*H*)-one (-)-**3**)

Prepared according to the procedure for 6(*S*)-**2G** from Pd₂(dba)₃ (4.6 mg, 5 mol%, 0.005 mmol), triphenylphosphine (5.8 mg, 22 mol%, 0.022 mmol), 1,2,3,6-tetra-*O*-acetyl-β-D-glucopyranose (35 mg, 0.1 mmol) and (-)-6-benzoyloxy-2*H*-pyran-3(6*H*)-one (-)-**3** (33 mg, 0.15 mmol) in DCM (2 ml) under Ar at -10 °C. After 16 h, purification of the residue (92% de, ¹H NMR) by flash column chromatography (SiO₂, EtOAc/hexane 3:7 to 1:1 gradient elution) gave product **6(*R*)-2H** (25 mg, 57%) as a colourless oil.

4-*O*-(6(*S*)-oxo-2*H*-pyran-3(6*H*)-one)-1,2,3,6-tetra-*O*-acetyl- β -D-glucopyranoside, **6(*S*)-2H**

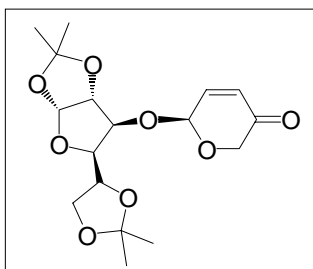
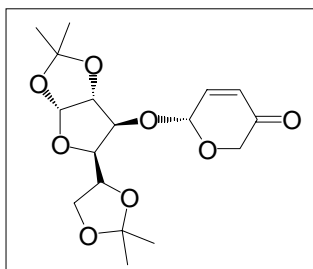
Spectra included: ^1H and ^{13}C NMR



(From (+)-6-Benzoyloxy-2*H*-pyran-3(6*H*)-one, (+)-**3**)

Prepared according to the procedure for **6(*S*)-2G** from $\text{Pd}_2(\text{dba})_3$ (4.6 mg, 5 mol%, 0.005 mmol), triphenylphosphine (5.8 mg, 22 mol%, 0.022 mmol), 1,2,3,6-tetra-*O*-acetyl- β -D-glucopyranose (35 mg, 0.1 mmol) and (+)-6-Benzoyloxy-2*H*-pyran-3(6*H*)-one (+)-**3** (33 mg, 0.15 mmol) in DCM (2 ml) under Ar at -10°C . After 16 h, purification of the residue (96% de, ^1H NMR) by flash column chromatography (SiO_2 , EtOAc/hexane 3:7 to 1:1 gradient elution) gave product **6(*S*)-2H** (27 mg, 61 %) as a colourless oil. $[\alpha]_D = -18.9^\circ$ (c 0.45, CH_2Cl_2). ^1H NMR (CDCl_3 , 300 MHz): δ 6.82 (dd, $J = 10.62$ and 3.66 Hz, 1H), 6.12 (d, $J = 10.25$ Hz, 1H), 5.71 (d, $J = 8.42$ Hz, 1H), 5.27 (dd, $J = 8.79$ and 8.79 Hz, 1 H), 5.15 (d, $J = 3.29$ Hz, 1 H), 5.06 (dd, $J = 8.42$ and 8.42 Hz, 1 H), 4.45 (dd, $J = 12.45$ and 3.66 Hz, 1 H), 4.36 (d, $J = 16.84$ Hz, 1 H), 4.26 (dd, $J = 12.08$ and 1.46 Hz, 1 H), 4.00 (d, $J = 16.84$ Hz, 1 H), 3.85 (dd, $J = 9.89$ and 9.89 Hz, 1 H), 3.76-3.72 (m, 1 H), 2.14 (s, 3 H), 2.11 (s, 3 H), 2.06 (s, 3 H) and 2.03 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3): 193.7, 170.7, 170.1, 169.5, 168.9, 142.9, 127.6, 95.2, 91.5, 76.6, 73.6, 73.6, 70.6, 66.7, 61.6, 20.8, 20.8, 20.8 and 20.6. MS (CI) for $\text{C}_{19}\text{H}_{24}\text{O}_{12}$: m/z 462 ($\text{M} + \text{NH}_4$) $^+$.

6-[5-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[2,3-*d*][1,3]dioxol-6-yloxy]-6*H*-pyran-3-one, **6(*R,S*)-2I**



Prepared according to the procedure for (\pm)-**2A** from palladium (II) acetate (5.6 mg, 5 mol%, 0.025 mmol), triphenylphosphite (11.1 mg, 11 mol%, 0.055 mmol), diacetone-D-glucose (130 mg, 0.5 mmol) and (\pm)-6-acetoxy-2*H*-pyran-3(6*H*)-one (\pm)-**1** (117 mg, 0.75 mmol) in DCM (2 ml). Purification of the residue by column chromatography

(SiO₂, 10-15% EtOAc/pentane, gradient elution) gave 2 diastereomers (crude ratio 2:3) of product **2I** (68 mg, 38% and 49 mg, 27 %) both as colourless oils:

Fraction 1 6(*R*)-[5-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[2,3-*d*][1,3]dioxol-6-yloxy]-6*H*-pyran-3-one, **6(*R*)-2I**

Spectra included: ¹H and ¹³C NMR

Anal. Calcd. for C₁₇H₂₄O₈: C, 57.30; H, 6.79%. Found: C, 57.4; H, 6.9. [α]_D = -44.8 (c 3.30, CH₂Cl₂). ¹H NMR (CDCl₃, 300 MHz) 6.85 (dd, *J* = 10.26 and 3.30 Hz, 1 H), 6.14 (d, *J* = 10.25 Hz, 1 H), 5.87 (d, *J* = 3.29 Hz, 1 H), 5.46 (d, *J* = 2.0 Hz, 1 H), 4.60 (d, *J* = 3.66 Hz, 1 H), 4.44 (d, *J* = 16.48 Hz, 1 H), 4.34 (s, 1 H), 4.20-4.08 (m, 4 H), 3.98 (m, 1 H), 1.50 (s, 3 H), 1.42 (s, 3 H), 1.35 (s, 3 H) and 1.32 (s, 3 H). ¹³C NMR (CDCl₃, 75 MHz) 193.8, 143.5, 128.0, 112.2, 109.4, 105.5, 94.7, 84.3, 82.1, 81.4, 72.7, 68.0, 66.6, 27.0, 26.9, 26.3 and 25.4. MS (CI) for C₁₇H₂₄O₈: *m/z* 374 (M + NH₄)⁺, 100%).

Fraction 2 6(*S*)-[5-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[2,3-*d*][1,3]dioxol-6-yloxy]-6*H*-pyran-3-one, **6(*S*)-2I**

Spectra included: ¹H and ¹³C NMR

[α]_D = - 3.5 (c 1.65, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃) 6.83 (dd, *J* = 10.25 and 3.30 Hz, 1 H), 6.14 (d, *J* = 10.62 Hz, 1 H), 5.88 (d, *J* = 3.66 Hz, 1 H), 5.35 (d, *J* = 3.30 Hz, 1 H), 4.74 (d, *J* = 17.2 Hz, 1 H), 4.54 (d, *J* = 3.66 Hz, 1 H), 4.47 (d, *J* = 2.93 Hz, 1 H), 4.28-4.21 (m, 1 H), 4.12-4.02 (m, 3 H), 3.94 (dd, *J* = 8.79 and 5.13 Hz, 1 H), 1.48 (s, 3 H), 1.39 (s, 3 H), 1.30 (s, 3 H) and 1.27 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃) 194.6, 143.1, 128.3, 112.0, 109.2, 105.2, 90.3, 82.4, 80.8, 77.9, 71.9, 67.6, 66.5, 26.8, 26.7, 26.1 and 25.3. MS (CI) for C₁₇H₂₄O₈: *m/z* 374 (M + NH₄)⁺, 100%).

6(*R*)-[5-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[2,3-*d*][1,3]dioxol-6-yloxy]-6*H*-pyran-3-one, **6(*R*)-2I**

(From (-)-6-Acetoxy-2*H*-pyran-3(6*H*)-one (-)-**1**)

Prepared according to the procedure for **6(*S*)-2G** from tris(dibenzylideneacetone)dipalladium (0) (4.6 mg, 5 mol%, 0.005 mmol), triphenylphosphine (5.8 mg, 22 mol%, 0.022 mmol), diacetone-D-glucose (26 mg, 0.1 mmol) and (-)-6-acetoxy-2*H*-pyran-3(6*H*)-one (-)-**1** (23 mg, 0.15 mmol) in DCM (2 ml) under argon at -20 °C. Purification of the residue (97% de,

¹H NMR) by column chromatography (SiO₂, 10-15% EtOAc/pentane, gradient elution) gave product **6(R)-2I** (25 mg, 70%) as a colourless oil.

(From (-)-6-Benzoyloxy-2*H*-pyran-3(6*H*)-one, (-)-**3**)

Prepared according to the procedure for **6(S)-2G** from tris(dibenzylideneacetone)dipalladium (0) (2.7 mg, 5 mol%, 0.003 mmol), triphenylphosphine (3.5 mg, 22 mol%, 0.013 mmol), diacetone-D-glucose (16 mg, 0.06 mmol) and (-)-benzoyloxy-2*H*-pyran-3(6*H*)-one (-)-**3** (20 mg, 0.09 mmol) in DCM (1.5 ml) under argon at -10 °C. Purification of the residue (82% de, ¹H NMR) by flash column chromatography (SiO₂, 10-15% EtOAc/pentane, gradient elution) gave product **6(R)-2I** (15 mg, 71%) as a colourless oil.

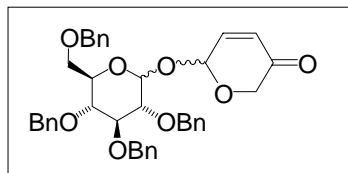
6(*S*)-[5-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[2,3-*d*][1,3]dioxol-6-yloxy]-6*H*-pyran-3-one, **6(S)-2I**

(From (+)-6-Benzoyloxy-2*H*-pyran-3(6*H*)-one, (+)-**3**)

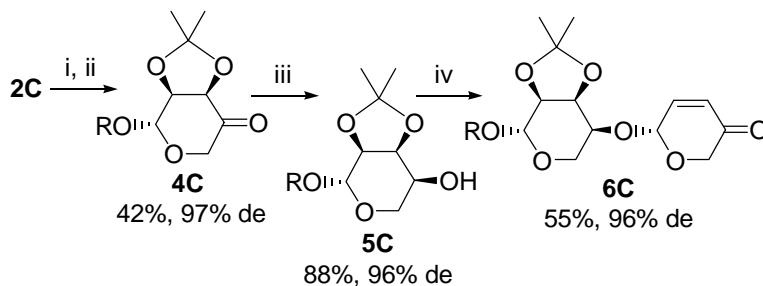
Prepared according to the procedure for **6(S)-2G** from tris(dibenzylideneacetone)dipalladium (0) (2.7 mg, 5 mol%, 0.003 mmol), triphenylphosphine (3.5 mg, 22 mol%, 0.013 mmol), diacetone-D-glucose (16 mg, 0.06 mmol) and (+)-benzoyloxy-2*H*-pyran-3(6*H*)-one (+)-**3** (20 mg, 0.09 mmol) in DCM (1.5 ml) under argon at -10 °C. Purification of the residue (95% de, ¹H NMR) by flash column chromatography (SiO₂, 10-15% EtOAc/pentane, gradient elution) gave product **6(S)-2I** (16 mg, 76%) as a colourless oil.

6-(3,4,5-Tris-benzyloxy-6-benzyloxymethyl-tetrahydro-pyran-2-yloxy)-6*H*-pyran-3-one, **2J**

Spectra included: ^1H and ^{13}C NMR



Prepared according to the procedure for (\pm)-**2A** from palladium (II) acetate (4.5 mg, 10 mol%, 0.02 mmol), triphenylphosphite (13.6 mg, 22 mol%, 0.044 mmol), 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (108 mg, 0.2 mmol) and (\pm)-6-acetoxy-2*H*-pyran-3(6*H*)-one (**1**) (94 mg, 0.6 mmol) in DCM (2 ml). Purification of the residue by column chromatography (SiO_2 , 5-15% acetone/pentane, gradient elution) gave 4 diastereomers (ratio 0.45(A):0.25(B):0.15(A):0.15(B)) of product **2J** (96 mg, 76%) as a colourless oil. ^1H NMR (CDCl_3 , 300 MHz) 7.36-7.22 (m, 18 H), 7.19-7.17 (m, 2 H), 6.99 (dd, $J = 10.62$ and 3.67 , 0.60 H diastereomers A), 6.84 (dd, $J = 10.25$ and 3.29 Hz, 0.15 H diastereomers B), 6.75 (dd, $J = 10.26$ and 3.30 Hz, 0.25 H diastereomers B), 6.23 (d, $J = 10.62$ Hz, 0.6 H diastereomers A), 6.18 (d, $J = 10.62$ Hz, 0.4 H diastereomers B), 5.71 (d, $J = 3.67$ Hz, 0.45 H diastereomers A), 5.53 (d, $J = 3.29$ Hz, 0.15 H diastereomers B), 5.48 (d, $J = 3.29$ Hz, 0.25 H diastereomers B), 5.37 (d, $J = 3.66$ Hz, 0.15 H diastereomers A), 5.04-4.41 (m, 10 H), 4.16-3.99 (m, 1 H), 3.76-3.68 (m, 4 H) and 3.58-3.53 (m, 2 H). ^{13}C NMR (CDCl_3 , 75 MHz) 194.3, 194.1, 143.9, 143.3, 143.0, 138.3, 137.9, 137.8, 137.7, 128.4, 128.3, 128.24, 128.16, 128.04, 127.97, 127.89, 127.86, 127.74, 127.68, 127.6, 102.2, 98.0, 94.0, 93.8, 89.0, 88.8, 84.8, 84.7, 82.4, 81.7, 81.6, 79.4, 77.5, 75.7, 75.6, 75.3, 75.2, 75.1, 75.0, 73.43, 73.37, 73.3, 71.2, 68.5, 68.4, 66.7, 66.4 and 66.2. MS (CI) for $\text{C}_{39}\text{H}_{40}\text{O}_8$: m/z 654 ($\text{M} + \text{NH}_4$) $^+$, 100%). HRMS ($\text{M}-\text{C}_7\text{H}_7$) calcd. for $\text{C}_{32}\text{H}_{33}\text{O}_8$: 545.21753. Found: 545.21851.



i. $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (20 mol%), NaIO_4 ; ii. 2,2-DMP, Acetone, PTSA; iii. $\text{Zn}(\text{BH}_4)_2$; iv. (\pm)-**1**, $\text{Pd}_2(\text{dba})_3$ (5 mol%), PPh_3 , CH_2Cl_2 .

4-(3-Methoxy-benzyloxy)-2,2-dimethyl-dihydro-[1,3]dioxolo[4,5-c]pyran-7-one, (\pm)-**4C**

To ruthenium (III) chloride trihydrate (65 mg, 0.25 mmol) under argon was added a solution of sodium metaperiodate (396 mg, 1.85 mmol) in water (3 ml). The resulting deep red solution was added *via* cannula to a solution of (\pm)-6-(3-methoxybenzyl)oxy-2*H*-pyran-3(6*H*)-one, (\pm)-**2C** (289 mg, 1.24 mmol) in a mixture of MeCN (9 ml) and EtOAc (9 ml) at -5°C under argon. After stirring the mixture for 25 min, a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (15 ml) was added and the mixture was extracted with EtOAc (3 x 20 ml). The organic layers were dried over Na_2SO_4 and concentrated to give the dihydroxy compound (276 mg) as a colourless wax which was protected directly as the dioxolane.

To a solution of the resulting dihydroxy compound in acetone (10 ml) was added 2,2-dimethoxypropane (1 ml) and *para*-toluenesulfonic acid (4 mg). After stirring for 2 h at ambient temperature the mixture was quenched with saturated aqueous NaHCO_3 (10 ml) and extracted with EtOAc (4 x 5 ml). The combined organic layers were dried over Na_2SO_4 and filtered. The solution was preadsorbed onto silica and purified by column chromatography (SiO_2 , acetone:pentane 1:9) to give the title compound (\pm)-**4C** (134 mg, 35%) as a colourless oil. Anal. Calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_6$: C, 62.33; H, 6.54%. Found: C, 62.10; H, 6.43. ^1H NMR (300 MHz, CDCl_3) 7.16-7.24 (m, 1 H), 6.79-6.85 (m, 3 H), 4.91 (s, 1 H), 4.69 (d, 1 H, $J = 12.09$ Hz), 4.50 (d, 1 H, $J = 12.08$ Hz), 4.41 (d, 1 H, $J = 6.95$ Hz), 4.37 (d, 1 H, $J = 6.95$ Hz), 4.17 (d, 1 H, $J = 16.48$ Hz), 4.10 (d, 1 H, $J = 16.48$ Hz), 3.75 (s, 3 H), 1.44 (s, 3 H) and 1.31 (s, 3 H). ^{13}C NMR (50.3 MHz, CDCl_3) 203.1, 159.8, 137.7, 129.6, 120.2, 113.6, 113.5, 111.9, 96.4, 77.7, 75.3, 69.8, 65.9, 55.2, 26.6 and 25.3. MS (EI): m/z 308 (M^+ , 10), and 121 ($\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2$, 100%). HRMS calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_6$: 308.12596. Found: 308.12658.

(+)-4-(3-Methoxy-benzyloxy)-2,2-dimethyl-dihydro-[1,3]dioxolo[4,5-c]pyran-7-one, (+)-**4C**

Prepared according to the procedure for (\pm)-**4C** from (-)-**2C** (234 mg, 1 mmol) to give (+)-**4C** (97% de, 130 mg, 42%). $[\alpha]_{\text{D}} = +79.6^{\circ}$ (97% de, c 3.40, CH_2Cl_2).

(\pm)-4-(3-Methoxy-benzyloxy)-2,2-dimethyl-dihydro-[1,3]dioxolo[4,5-c]pyran-7-ol, (\pm)-**5C**

To a solution of (\pm)-**4C** (48 mg, 0.156 mmol) in THF (4 ml) at -20°C under argon was added zinc borohydride (0.313 ml, 0.156 mmol, 0.5 M in diethyl ether). The resulting mixture was stirred for 15 min and H_2O (4 ml) was added. Following extraction with CH_2Cl_2 (3 x 5 ml), drying over Na_2SO_4 and concentration *in vacuo*, the residue was purified by chromatography (SiO_2 , acetone/pentane 1:4) to give the title compound (\pm)-**5C** (40 mg, 83%) as a colourless waxy solid. ^1H NMR (200 MHz, CDCl_3) 7.29-7.22 (m, 1 H), 6.94-6.80 (m, 3 H), 4.77 (d, 1 H, $J = 11.96$ Hz), 4.77 (d, 1 H, $J = 3.17$

Hz), 4.54 (d, 1 H, $J = 11.96$ Hz), 4.41 (dd, 1 H, $J = 4.15$ and 6.35 Hz), 4.14 (dd, 1 H, $J = 3.41$ and 6.34 Hz), 4.05 (m, 1 H), 3.84 (dd, 1 H, $J = 4.39$ and 10.98 Hz), 3.80 (s, 3 H), 3.61 (dd, 1 H, $J = 8.06$ and 11.23 Hz), 2.26 (d, 1 H, $J = 8.55$ Hz), 1.49 (s, 3 H) and 1.37 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3) 159.6, 138.7, 129.4, 120.2, 113.4, 113.3, 109.9, 97.7, 75.1, 73.0, 69.5, 64.2, 62.4, 55.2, 27.5 and 25.3. MS (EI): m/z 310 (M^+ , 2%), 295 (MH-O, 9), 189 (M- $\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2$, 32) and 121 ($\text{CH}_3\text{OC}_6\text{H}_4\text{CH}_2$, 100). HRMS calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_6$: 310.14161. Found: 310.14240.

(+)-4-(3-Methoxy-benzyloxy)-2,2-dimethyl-dihydro-[1,3]dioxolo[4,5-c]pyran-7-ol, (+)-**5C**

Spectra included: ^1H and ^{13}C NMR

Prepared according to the procedure for (\pm)-**5C** from (+)-**4C** (100 mg, 0.32 mmol) to give (+)-**5C** (96% de, 88 mg, 88%).

$[\alpha]_{\text{D}} = +83.6^\circ$ (96% de, c 3.2, CH_2Cl_2)

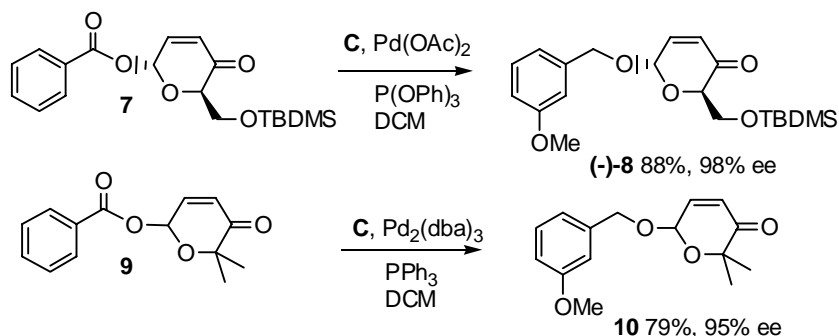
6-[4-(3-Methoxy-benzyloxy)-2,2-dimethyl-tetrahydro-[1,3]dioxolo[4,5-c]pyran-7-yloxy]-6H-pyran-3-one, **6(R,S)-6C**

Prepared according to the procedure for (\pm)-**2A** from palladium (II) acetate (1.5 mg, 10 mol%, 0.0065 mmol), triphenylphosphite (4.4 mg, 22 mol%, 0.014 mmol), (\pm)-**5C** (20 mg, 0.0065 mmol) and (\pm)-benzoyloxypyranone (\pm)-**3** (21 mg, 0.097 mmol) in DCM (1 ml). Purification of the residue by column chromatography (SiO_2 , 25-30% EtOAc/pentane gradient elution) gave 2 diastereomers of product **6C** (15 mg, 58%) as a colourless oil. ^1H NMR (300 MHz, CDCl_3) 7.23-7.29 (m, 1 H), 6.83-6.94 (m, 4 H), 6.15 (d, $J = 10.62$ Hz, 1 H), 5.40 (d, $J = 3.30$ Hz, 0.35 H, *diastereomer 1*), 5.34 (d, $J = 2.93$ Hz, 0.65 H, *diastereomer 2*), 4.81-4.07 (m, 8 H), 3.91-3.69 (m, 2 H), 3.81 (s, 3 H), 1.47 (s, 1.05 H, *diastereomer 1*), 1.44 (s, 1.95 H, *diastereomer 2*) and 1.36 (s, 3 H, *diastereomers 1 and 2*). ^{13}C NMR (75 MHz, CDCl_3) 194.3, 194.0, 159.7, 143.6, 143.3, 138.7, 129.4, 128.2, 120.23, 120.17, 113.5, 113.42, 113.36, 110.7, 110.5, 98.8, 98.3, 93.6, 93.1, 75.9, 75.8, 73.7, 72.0, 71.7, 71.0, 69.9, 69.8, 66.4, 66.3, 61.2, 60.3, 55.2, 27.0, 26.8 and 25.5. MS (EI): m/z 406 (M^+ , 1%), 391 (M- CH_3 , 1), 285 (M-MeOBn, 3), 121 (Bn, 57) and 97 ($\text{C}_5\text{H}_5\text{O}_2$, 100). HRMS calcd. for $\text{C}_{21}\text{H}_{26}\text{O}_8$: 406.16275. Found: 406.16288.

(+)-6(*R*)-[4-(3-Methoxy-benzyloxy)-2,2-dimethyl-tetrahydro-[1,3]dioxolo[4,5-*c*]pyran-7-yl]oxy]-6H-pyran-3-one, **6(*R*)-6C**

Spectra included: ^1H and ^{13}C NMR

Prepared according to the procedure for 6(*S*)-(-)-**2G** from tris(dibenzylideneacetone)dipalladium (0) (3.3 mg, 5 mol%, 0.0035 mmol), triphenylphosphine (4.1 mg, 22 mol%, 0.016 mmol), (+)-**5C** (22 mg, 0.071 mmol) and (-)-6-acetoxy-2*H*-pyran-3(6*H*)-one (-)-**1** (17 mg, 0.11 mmol) in DCM (2.5 ml) under argon at -10°C . Purification of the residue (96% de by ^1H NMR) by column chromatography (SiO_2 , 5-10% acetone/pentane, gradient elution) gave product **6(*R*)-6C** (16 mg, 55 %) as a colourless oil. $[\alpha]_{\text{D}}^{20} = +3.2^\circ$ (c 0.73, CH_2Cl_2). ^1H NMR (300 MHz, CDCl_3) 7.23-7.29 (m, 1 H), 6.83-6.94 (m, 4 H), 6.15 (d, $J = 10.25$ Hz, 1 H), 5.34 (d, $J = 3.29$ Hz, 1 H), 4.79 (d, $J = 12.08$ Hz, 1 H), 4.70-4.56 (m, 4 H), 4.34-4.27 (m, 1 H), 4.13-4.07 (m, 2 H), 3.87-3.68 (m, 2 H), 3.81 (s, 3 H), 1.44 (s, 3 H) and 1.37 (s, 3 H). ^{13}C NMR (75 MHz, CDCl_3) 194.3, 159.7, 143.3, 138.7, 129.5, 128.2, 120.2, 113.41, 113.36, 110.5, 98.8, 93.6, 75.9, 73.7, 71.7, 69.9, 66.4, 60.3, 55.2, 27.0 and 25.5. MS (EI): m/z 406 (M^+ , 1%), 391 ($\text{M}-\text{CH}_3$, 3), 285 ($\text{M}-\text{MeOBn}$, 3), 121 (Bn, 54) and 97 ($\text{C}_5\text{H}_5\text{O}_2$, 100). HRMS calcd. for $\text{C}_{21}\text{H}_{26}\text{O}_8$: 406.16275. Found: 406.16199.



2-(*tert*-Butyl-dimethyl-silyloxymethyl)-6-(3-methoxy-benzyloxy)-6H-pyran-3-one, (\pm)-**8**

To palladium (II) acetate (0.8 mg, 5 mol%, 3.5 μmol) in a flame-dried Schlenk tube under argon was added a solution of triphenylphosphite (2.4 mg, 11 mol%, 7.6 μmol) in DCM (1.5 ml) *via* cannula. After stirring the yellow solution at ambient temperature for 10 min, 3-methoxybenzyl alcohol (14.3 mg, 13 μl , 0.104 mmol) was added *via* microsyringe. After further stirring for 10 min (\pm)-6-(*tert*-butyldimethylsilyloxymethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl benzoate (\pm)-**7** (25 mg, 0.069 mmol) was added as a solid and the mixture was stirred in the dark for 24 h. The homogeneous orange solution was preadsorbed on silica and purified by flash column chromatography (SiO_2 , acetone:pentane 4:96) to

give the title compound (19 mg, 73%) as a colourless oil. ^1H NMR (300 MHz, CDCl_3) 7.31-7.26 (m, 1 H), 6.97-6.85 (m, 4 H), 6.12 (d, 1 H, $J = 10.25$ Hz), 5.40 (d, 1 H, $J = 3.30$ Hz), 4.85 (d, 1 H, $J = 11.72$ Hz), 4.75 (d, 1 H, $J = 11.72$ Hz), 4.50 (dd, 1 H, $J = 5.12$ and 2.56 Hz), 4.10-4.00 (m, 2 H), 3.82 (s, 3 H) 0.89 (s, 9 H) and 0.09 (s, 6 H). ^{13}C NMR (75 MHz, CDCl_3) 194.6, 159.8, 143.7, 138.6, 129.6, 128.3, 120.4, 113.62, 113.57, 92.0, 76.2, 70.3, 62.5, 55.2, 25.8, 18.3, -5.3 and -5.4. MS (CI) for $\text{C}_{20}\text{H}_{30}\text{O}_5\text{Si}$: m/z 396 ($\text{M} + \text{NH}_4$) $^+$, 100% and 379 (MH, 50). HRMS ($\text{M} - \text{CH}_3$) calcd. for $\text{C}_{19}\text{H}_{27}\text{O}_5\text{Si}$: 363.16276. Found: 363.16382.

(-)-2(*R*)-(tert-Butyl-dimethyl-silanyloxymethyl)-6(*S*)-(3-methoxy-benzyloxy)-6*H*-pyran-3-one (**2R,6S**)-8

Spectra included: ^1H and ^{13}C NMR

To palladium (II) acetate (1.6 mg, 10 mol%, 6.9 μmol) in a flame-dried Schlenk tube under argon was added a solution of triphenylphosphite (4.7 mg, 22 mol%, 15.2 μmol) in DCM (1.5 ml) *via* cannula. After stirring the yellow solution at ambient temperature for 10 min, 3-methoxybenzyl alcohol (14.3 mg, 13 μl , 0.104 mmol) was added *via* microsyringe. After further stirring for 10 min and cooling to -10°C , (-)-6-(tert-butyl-dimethyl-silanyloxymethyl)-5-oxo-5,6-dihydro-2*H*-pyran-2-yl benzoate (**2R,6R**)-7 (25 mg, 0.069 mmol) was added as a solid and the mixture was stirred in the dark for 24 h. The homogeneous orange solution was preadsorbed on silica and purified by flash column chromatography (SiO_2 , acetone:pentane 4:96) to give the title compound (23 mg, 88%) as a colourless oil. $[\alpha]_{\text{D}} = -38.6^\circ$ (c 0.12, CH_2Cl_2)

Benzoic acid 6,6-dimethyl-5-oxo-5,6-dihydro-2*H*-pyran-2-yl ester, (\pm)-9

The racemate (\pm)-9 was prepared according to a literature procedure and was resolved by preparative HPLC on a Chiralcel OD column, *iso*-propanol:heptane 1:99 (RTs 10.1 and 11.5 min)

Fraction 1, (-)-9: 99% ee, $[\alpha]_{\text{D}} = -277.8^\circ$ (c 0.63, CHCl_3)

(\pm)-6-(3-Methoxy-benzyloxy)-2,2-dimethyl-pyran-3(6*H*)-one, (\pm)-10

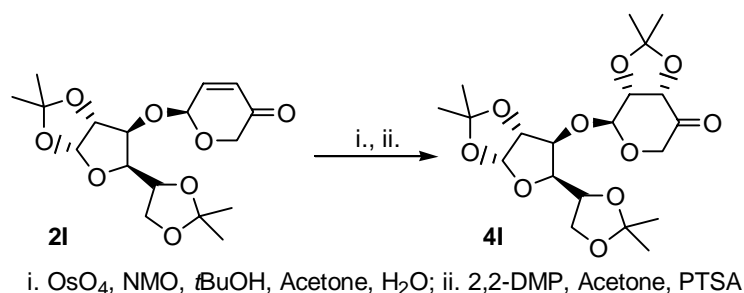
Prepared according to the procedure for (\pm)-2A from palladium (II) acetate (6.8 mg, 5 mol%, 0.03 mmol), triphenylphosphite (20.5 mg, 11 mol%, 0.066 mmol), 3-methoxybenzyl alcohol (55 mg, 50 μl , 0.4 mmol) and (\pm)-6-acetoxy-2,2-dimethyl-pyran-3(6*H*)-one (110 mg, 0.6 mmol) in DCM (3 ml). Purification of the residue by column chromatography (SiO_2 , acetone:pentane 1:19) gave product (\pm)-10 (83 mg, 79%) as a colourless oil. ^1H NMR (300 MHz,

CDCl₃) 7.29-7.23 (m, 1 H), 6.94-6.80 (m, 4 H), 6.05 (d, 1 H, $J = 10.26$ Hz), 5.34 (d, 1 H, $J = 2.92$ Hz), 4.88 (d, 1 H, $J = 11.72$ Hz), 4.60 (d, 1 H, $J = 11.72$ Hz), 3.79 (s, 3 H), 1.54 (s, 3 H) and 1.39 (s, 3 H). ¹³C NMR (75 MHz, CDCl₃) 199.3, 159.8, 143.9, 138.7, 129.6, 126.3, 120.3, 113.5, 113.4, 92.1, 79.3, 69.7, 55.2, 27.0 and 24.9. MS (EI): m/z 262 (M⁺, 1%), 204 (M-C₃H₆O, 3%). HRMS calcd. for C₁₅H₁₈O₄: 262.12049. Found: 262.12134.

(-)-6-(3-Methoxy-benzyloxy)-2,2-dimethyl-pyran-3(6*H*)-one, (-)-**10**

Spectra included: ¹H and ¹³C NMR

Prepared according to the procedure for **6(S)-2G** from tris(dibenzylideneacetone)dipalladium (0) (2.5 mg, 5 mol%, 0.0027 mmol), triphenylphosphine (3.1 mg, 22 mol%, 0.0119 mmol), 3-methoxybenzyl alcohol (7.5 mg, 6.7 μ l, 0.054 mmol) and (-)-6-benzoyloxy-2,2-dimethyl-pyran-3(6*H*)-one (-)-**9** (20 mg, 0.08 mmol) in DCM (1.5 ml) under argon at -10 °C. Purification of the residue by flash column chromatography (SiO₂, 5% EtOAc/pentane) gave product (-)-**10** (11 mg, 79%, 95% ee) as a colourless oil. $[\alpha]_D = -17.3^\circ$ (c 0.55, CHCl₃).



4-[5-(2,2-Dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[2,3-*d*][1,3]dioxol-6-yloxy]-2,2-dimethyl-dihydro-[1,3]dioxolo[4,5-*c*]pyran-7-one, **4I**

Spectra included: ¹H and ¹³C NMR

To a solution of (-)-6-[5-(2,2-dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyl-tetrahydro-furo[2,3-*d*][1,3]dioxol-6-yloxy]-6*H*-pyran-3-one **6(S)-(-)-2I** (16 mg, 0.045 mmol) in acetone (0.4 ml) and *tert*-butanol (0.4 ml) was added a molar excess of a 1:1 (w/w) solution of 4-methylmorpholine-*N*-oxide (12 mg, 0.09 mmol) in water. The solution was cooled to 0 °C and a catalytic amount (2 mol%) of OsO₄ was added. After stirring for 6 h the mixture was quenched with Na₂SO₃ sat. aq., extracted with EtOAc (4 x 5 ml) dried over Na₂SO₄ and concentrated. The crude mixture containing the dihydroxylated product was submitted to the following conditions without further purification.

To a solution of the residue obtained from dihydroxylation in acetone (1 ml) was added 2,2-dimethoxypropane (0.1 ml) and a catalytic amount of PTSA (5 mol%). The mixture was stirred at ambient temperature for 16 h. Quenching of the reaction with Na₂HCO₃ sat. aq., extraction with EtOAc (3 x 5 ml), drying over Na₂SO₄, concentration and purification by

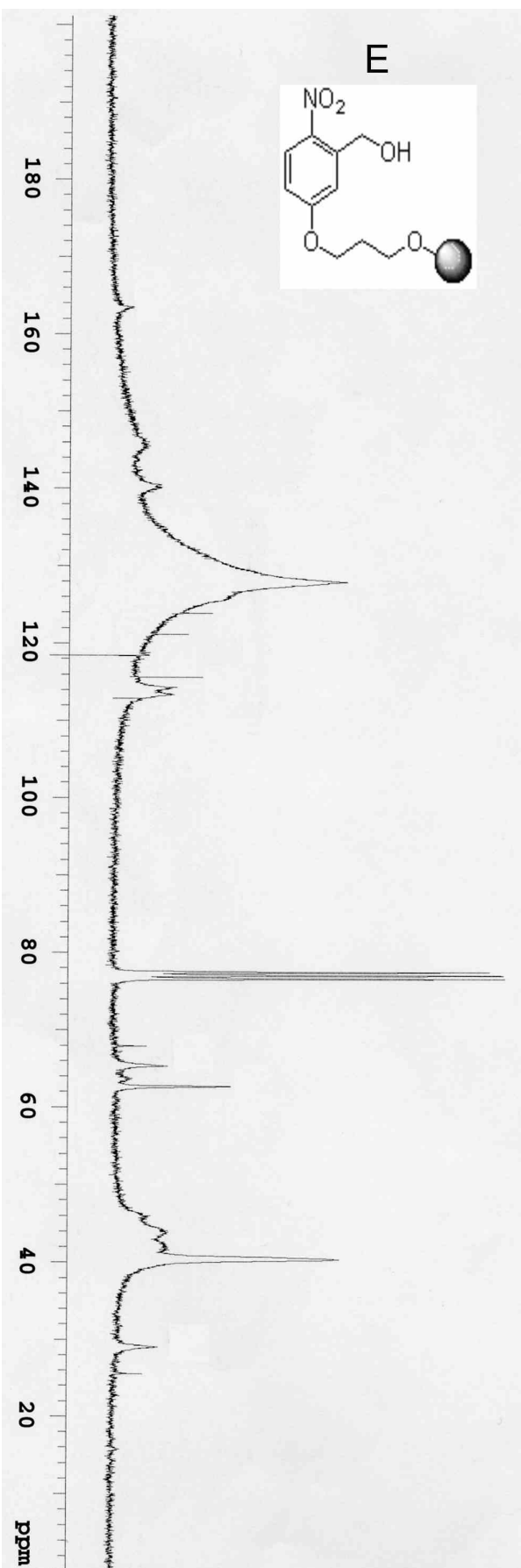
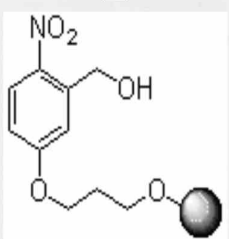
flash column chromatography (SiO₂, 5% acetone/pentane) gave the title compound **4I** (0.8 mg, 4%) as a colourless oil. ¹H NMR (CDCl₃, 300 MHz) 5.88 (d, *J* = 3.66 Hz, 1 H), 5.12 (s, 1 H), 4.61-4.55 (m, 2 H), 4.40-4.36 (m, 3 H), 4.23-4.07 (m, 4H), 3.95 (dd, *J* = 8.43 and 4.76 Hz, 1 H), 1.52 (s, 3 H), 1.51 (s, 3 H), 1.41 (s, 3 H), 1.38 (s, 3 H) and 1.32 (s, 6 H). ¹³C NMR (75 MHz, CDCl₃) 203.0, 118.5, 112.2, 109.5, 105.1, 94.9, 81.8, 80.7, 77.6, 77.5, 75.1, 71.5, 67.7, 65.8, 26.8, 26.7, 26.7, 26.1, 25.4 and 25.1. MS (CI) for C₂₀H₃₀O₁₀: *m/z* 448 (M + NH₄)⁺, 81%) and 431 (MH⁺, 100).

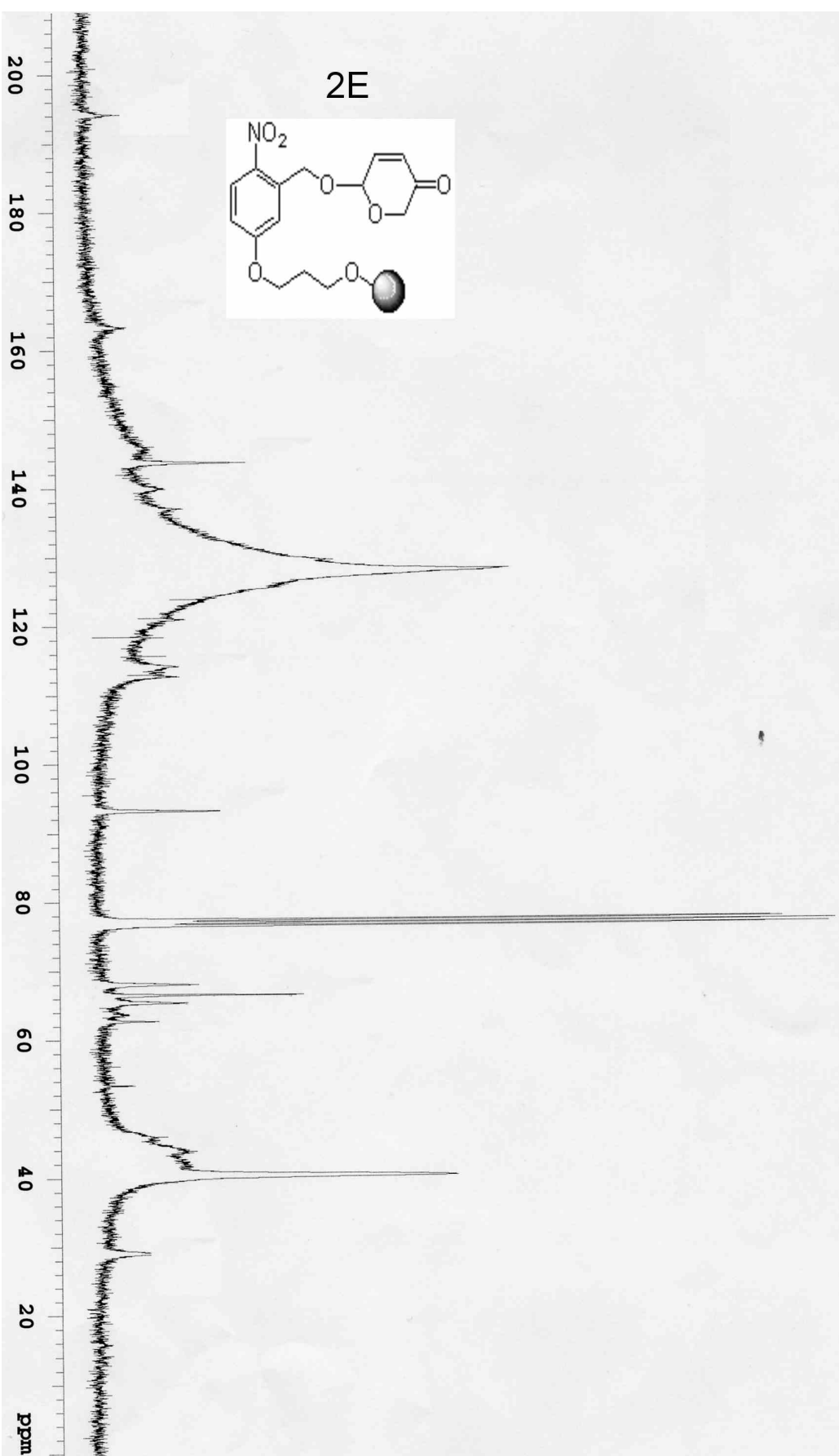
Chiral chromatography data

Compound	GC/ HPLC	Column	Eluent	Retention times min ⁻¹	de/ee %
(±)- 1	GC	Lipodex C, 50 m x 0.25mm ID	95 °C oven, Flow Rate 1.3 mlmin ⁻¹	26.1 and 27.4	rac
(-)- 1	GC	Lipodex C, 50 m x 0.25mm ID	95 °C oven, Flow Rate 1.3 mlmin ⁻¹	27.4	>99
(±)- 2A	HPLC	Chiralpak AD	95/5 heptane/IPA	6.9 and 7.9	rac
2A	HPLC	Chiralpak AD	95/5 heptane/IPA	7.9	94
(±)- 2B	HPLC	Chiralpak AD	99/1 heptane/IPA	26.6 and 31.6	rac
(-)- 2B	HPLC	Chiralpak AD	99/1 heptane/IPA	31.6	98*
(±)- 2C	HPLC	Chiralpak AD	99/1 heptane/IPA	23.0 and 28.3	rac
(-)- 2C	HPLC	Chiralpak AD	99/1 heptane/IPA	28.3	99
(±)- 2D	HPLC	Chiralcel OD	90/10 heptane/IPA	10.7 and 11.7	rac
(-)- 2D	HPLC	Chiralcel OD	90/10 heptane/IPA	11.7	98
2F	HPLC	Chiralpak AS	90/10-60/40 hep/IPA	23.2 and 26.1	2 x diast.
(-)- 2F	HPLC	Chiralpak AS	90/10-60/40 hep/IPA	26.1	97
(±)- 3	HPLC	Chiralpak AS	90/10 heptane/IPA	8.3 and 10.7	rac
(+)- 3	HPLC	Chiralpak AS	90/10 heptane/IPA	8.3	99
(-)- 3	HPLC	Chiralpak AS	90/10 heptane/IPA	10.7	99
(±)- 4C	HPLC	Chiralcel OD	95/5 heptane/IPA	16.1 and 19.1	98 de
(+)- 4C	HPLC	Chiralcel OD	95/5 heptane/IPA	19.1	97 de

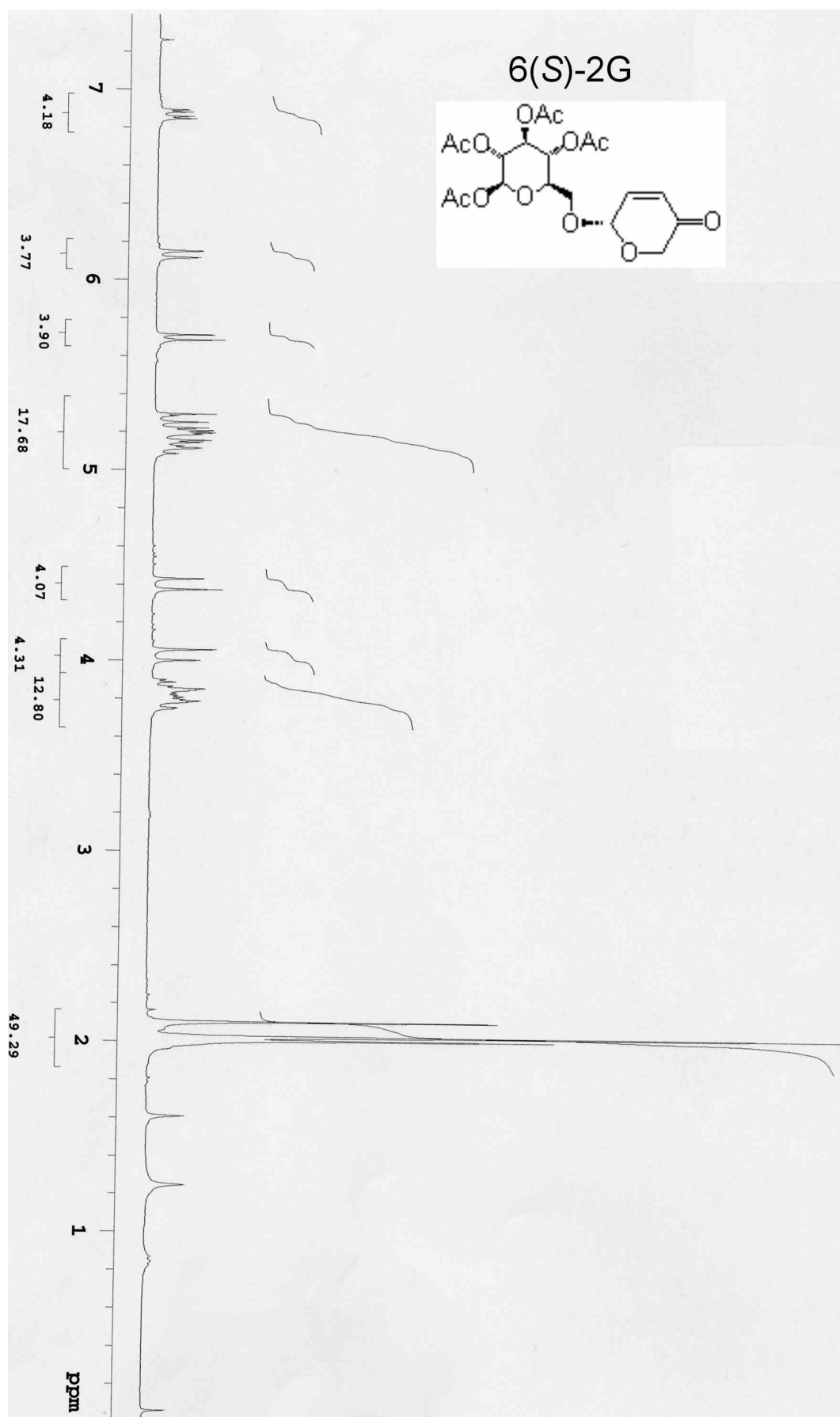
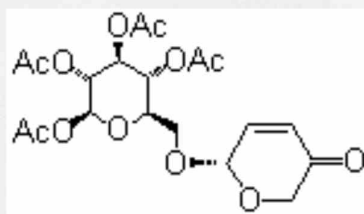
(±)-5C	HPLC	Chiralcel OD	90/10 heptane/IPA	10.9 and 14.8	98 de
(+)-5C	HPLC	Chiralcel OD	90/10 heptane/IPA	14.8	96 de
(±)-7	HPLC	Chiralcel OD	99/1 heptane/IPA	10.6 and 11.9	rac
7	HPLC	Chiralcel OD	99/1 heptane/IPA	10.6	99
(±)-9	HPLC	Chiralcel OD	99/1 heptane/IPA	10.1 and 11.5	rac
(-)-9	HPLC	Chiralcel OD	99/1 heptane/IPA	10.1	99
(±)-10	HPLC	Chiralpak AD	99/1 heptane/IPA	10.1 and 11.2	rac
(±)-10	HPLC	Chiralpak AD	99/1 heptane/IPA	11.2	95

*before flash column chromatography (SiO₂)

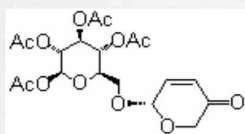




6(S)-2G



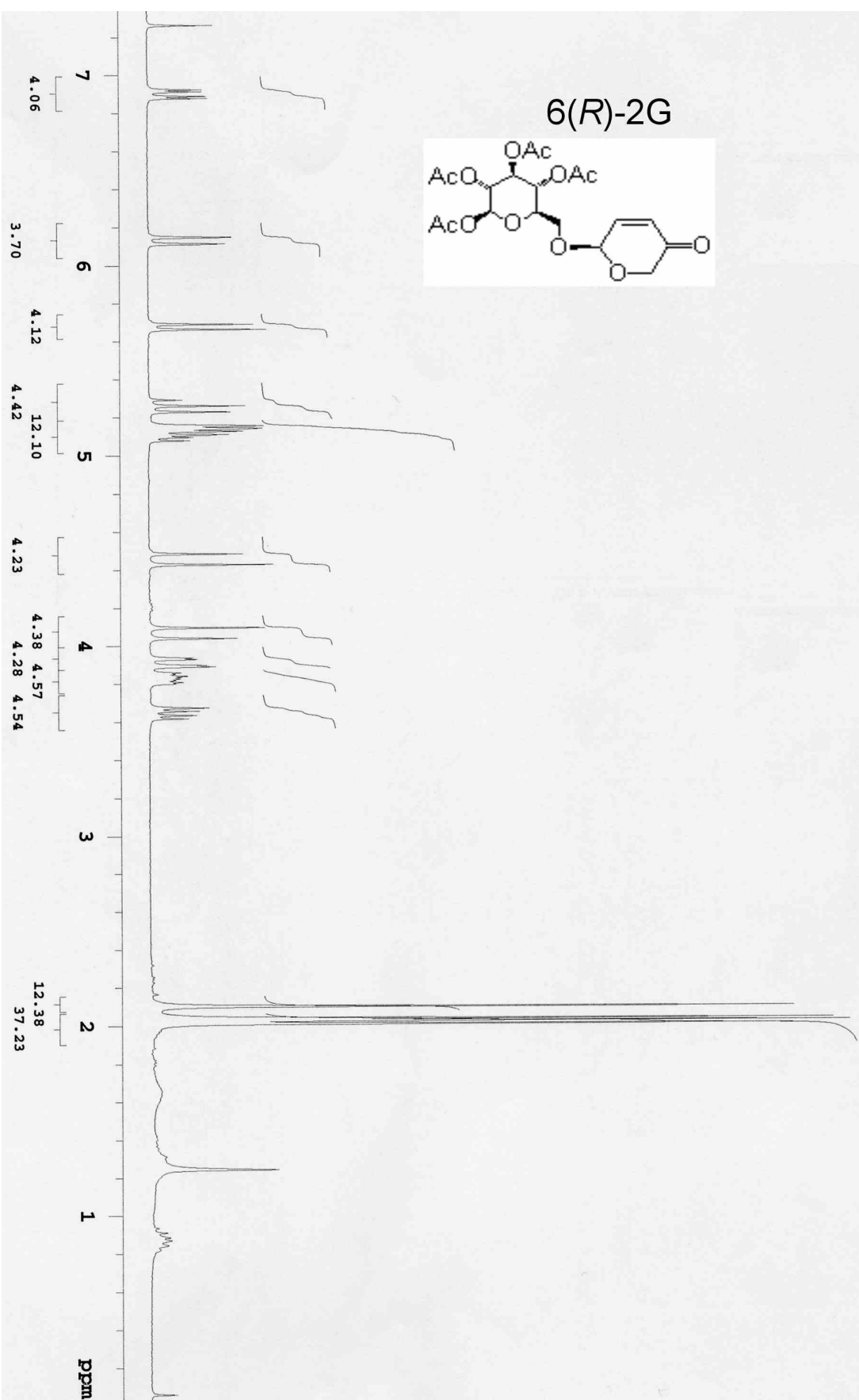
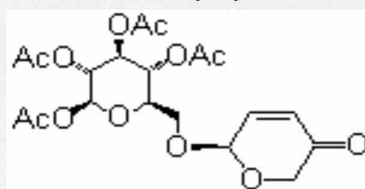
6(S)-2G

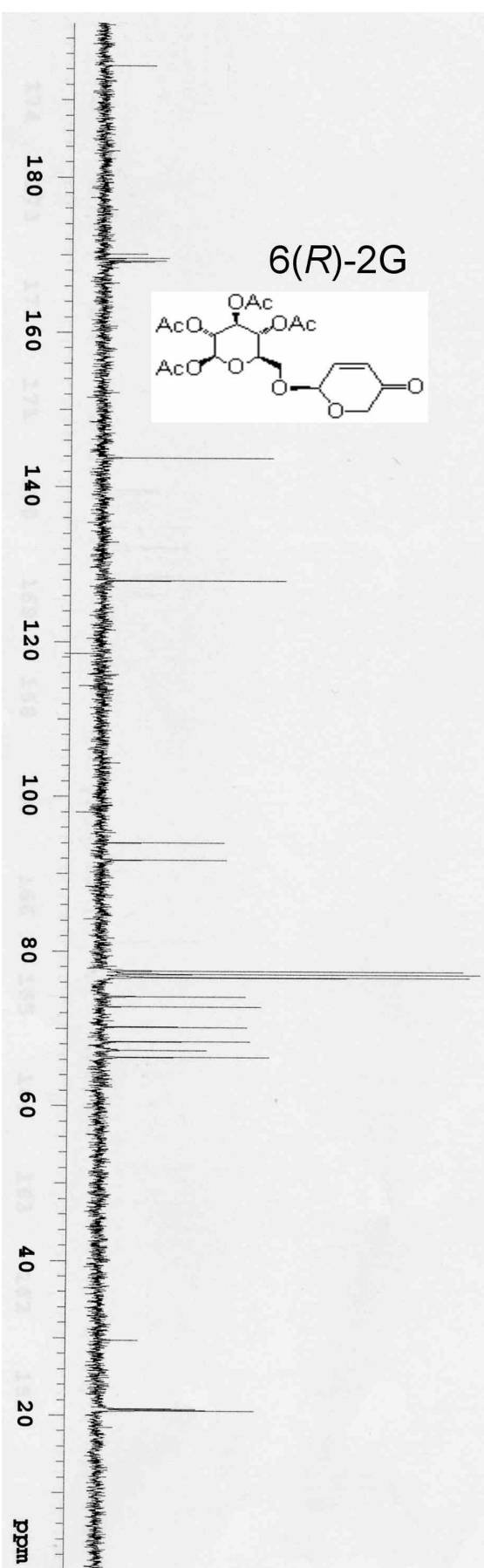


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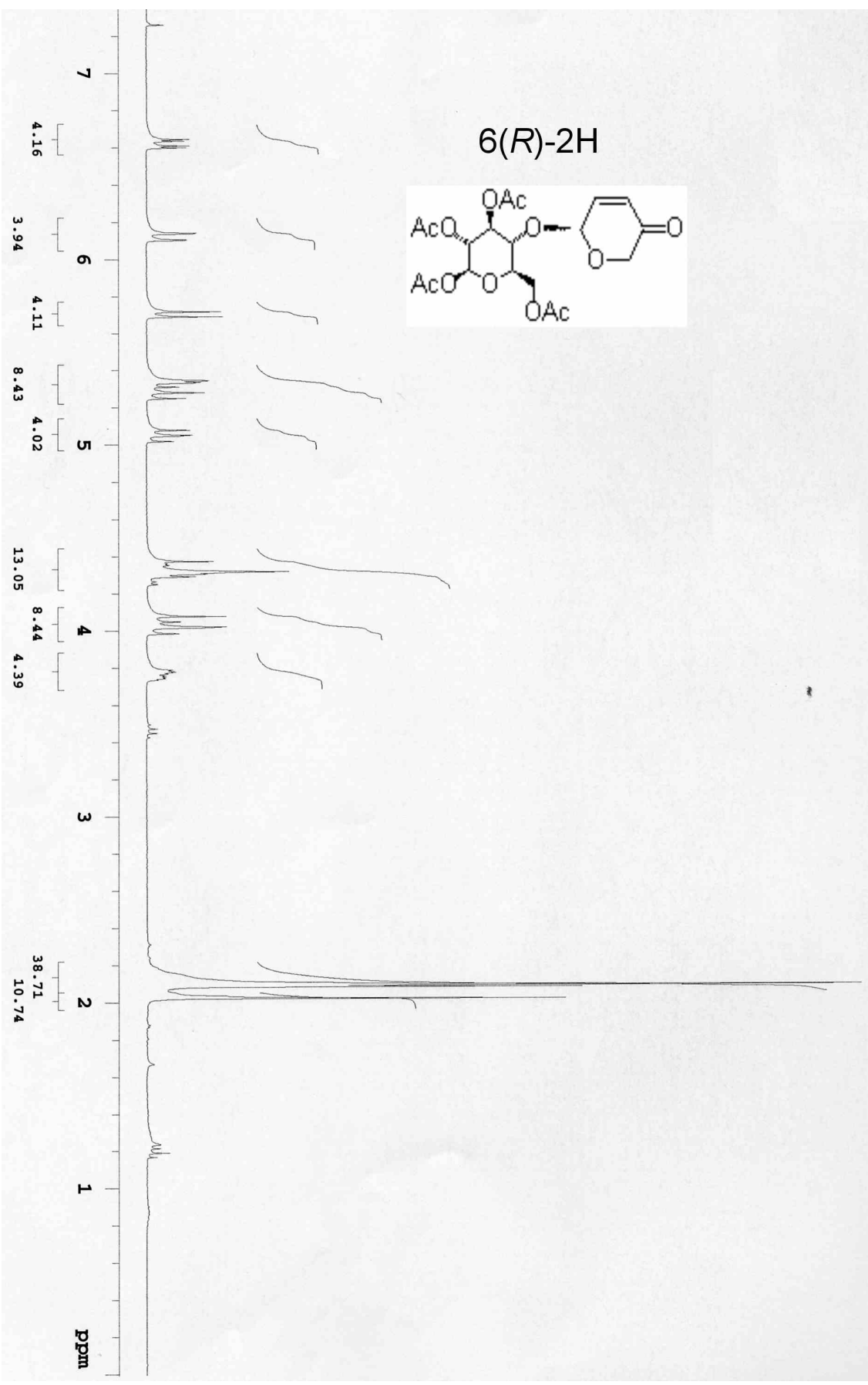
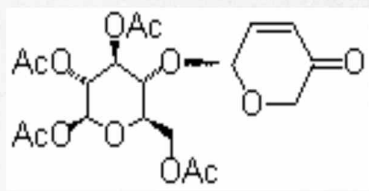


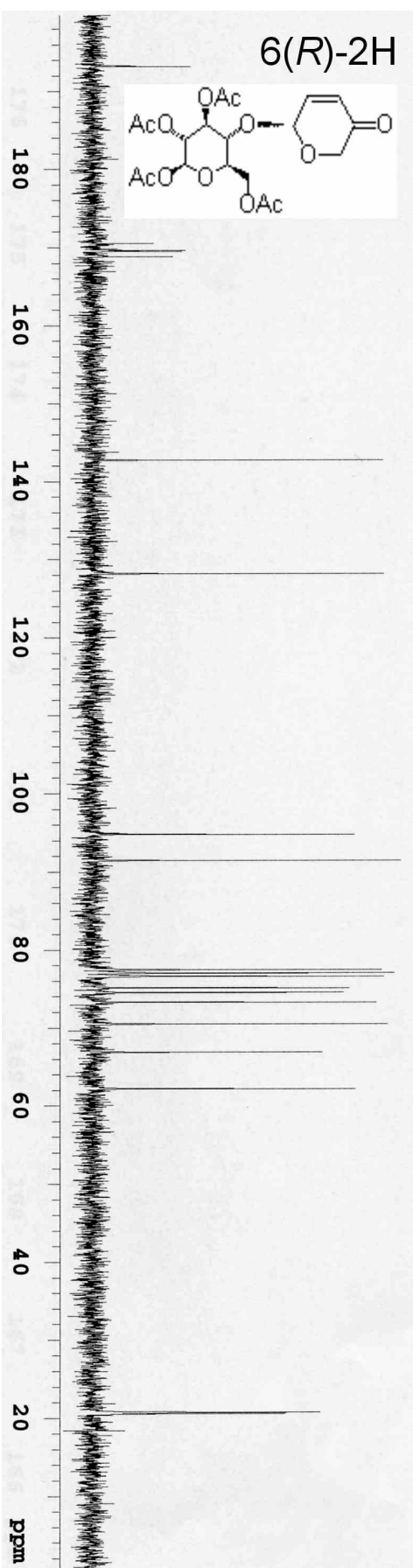
6(*R*)-2G



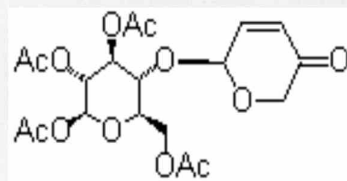


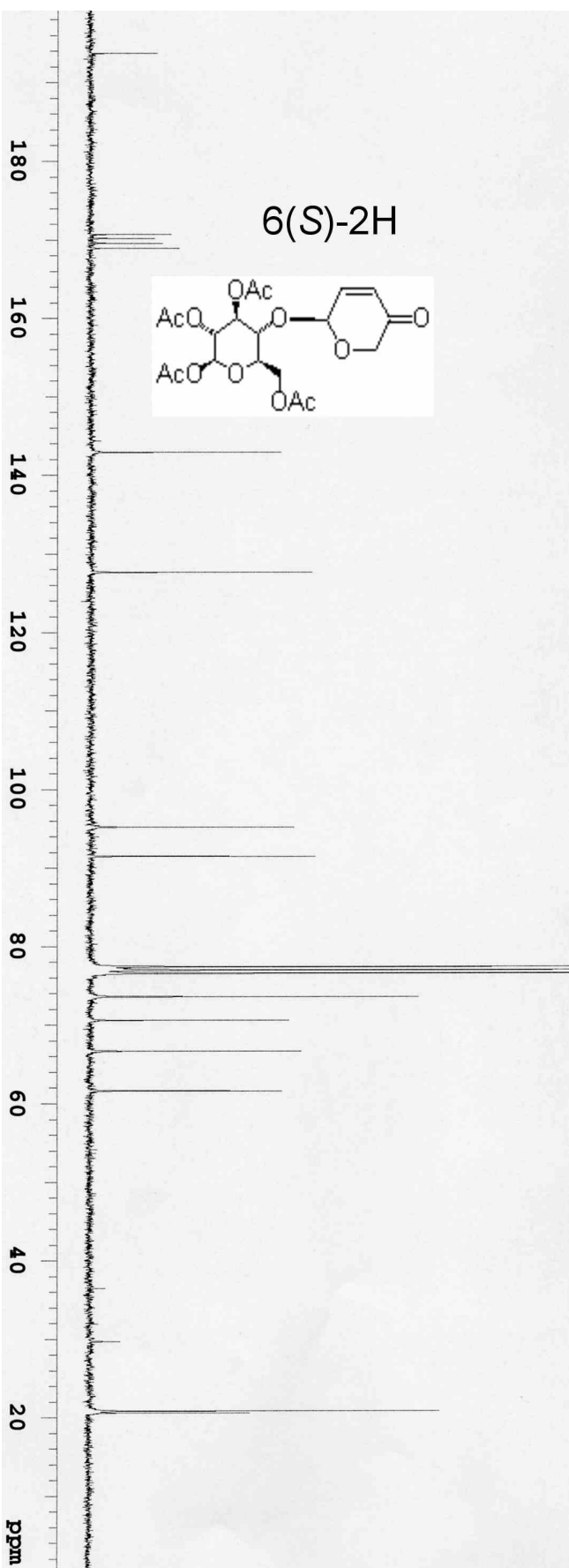
6(R)-2H



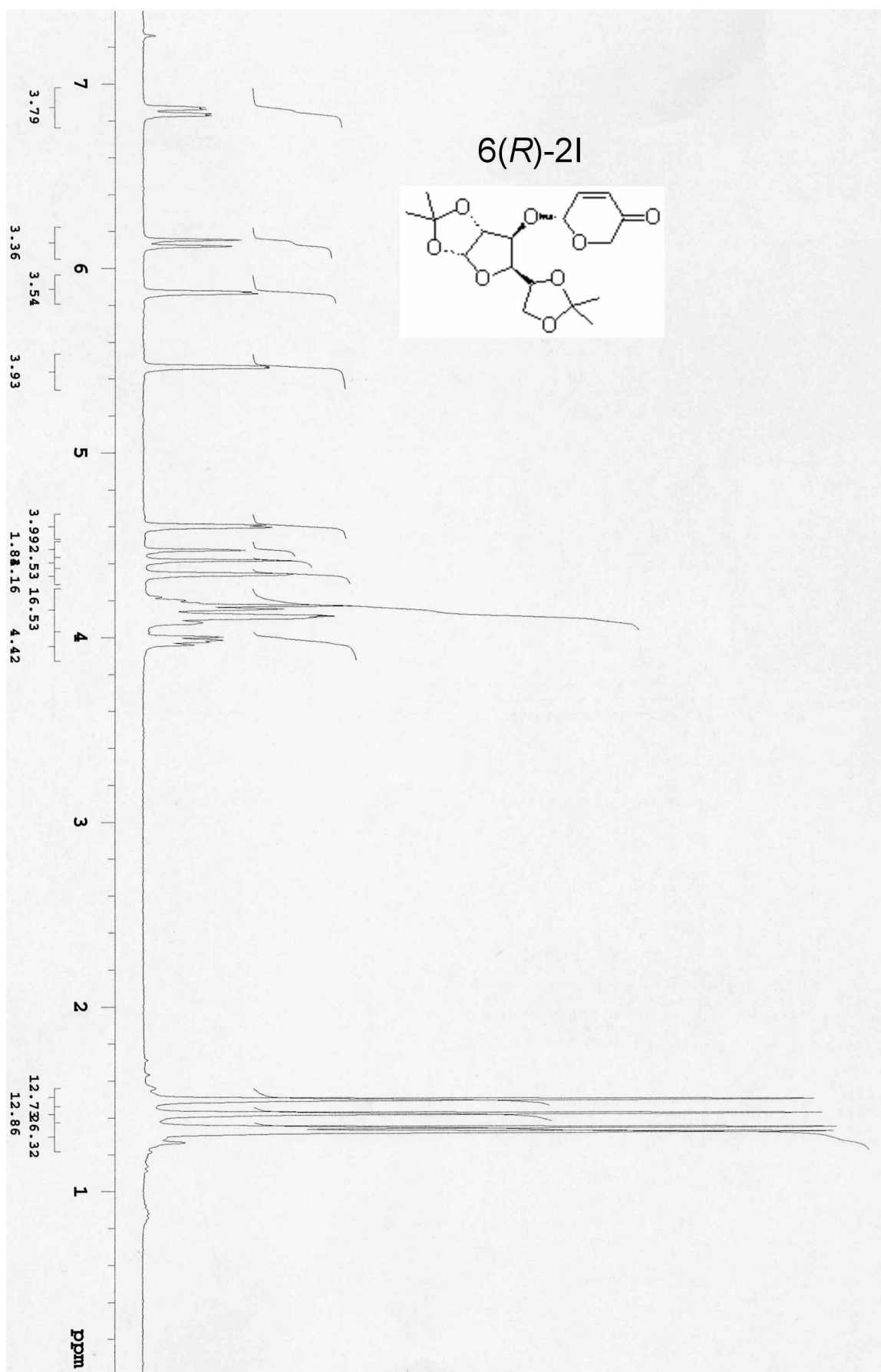
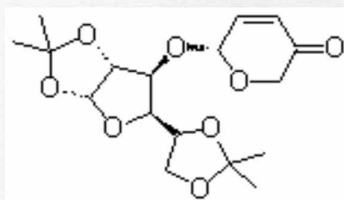


6(S)-2H

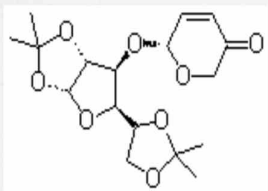




6(*R*)-2I



6(*R*)-21



180

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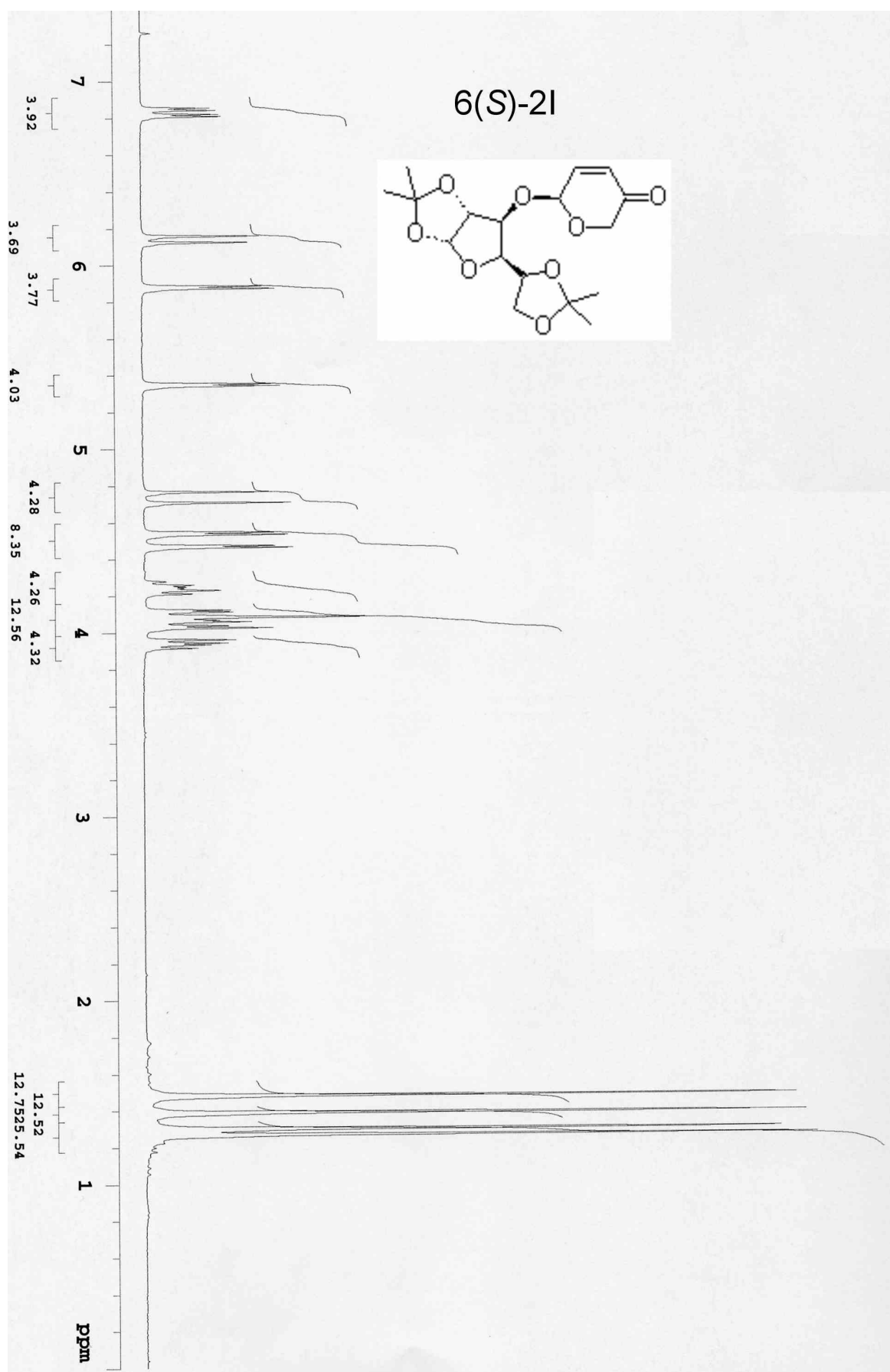
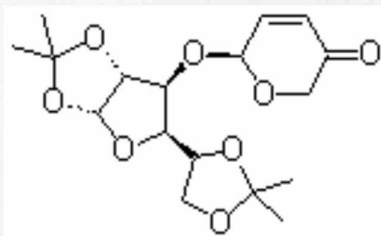
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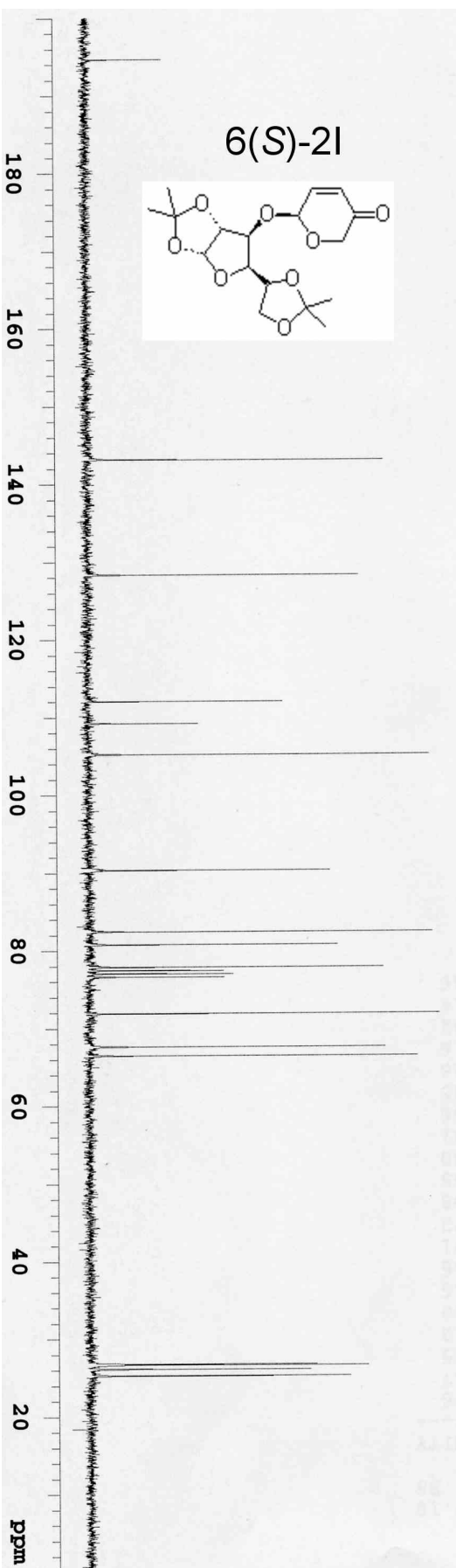
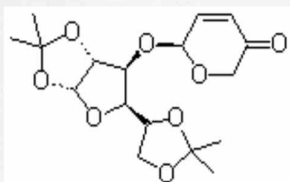
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ppm

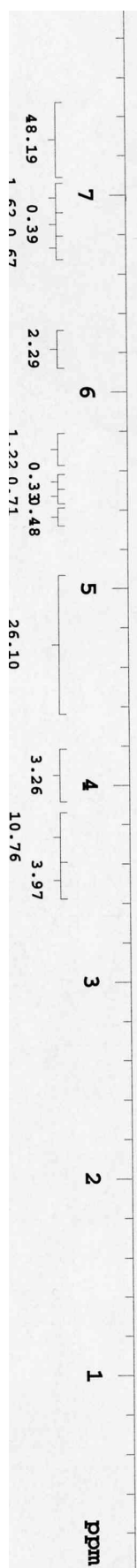
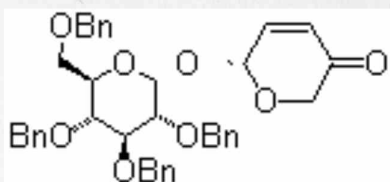
6(S)-2I

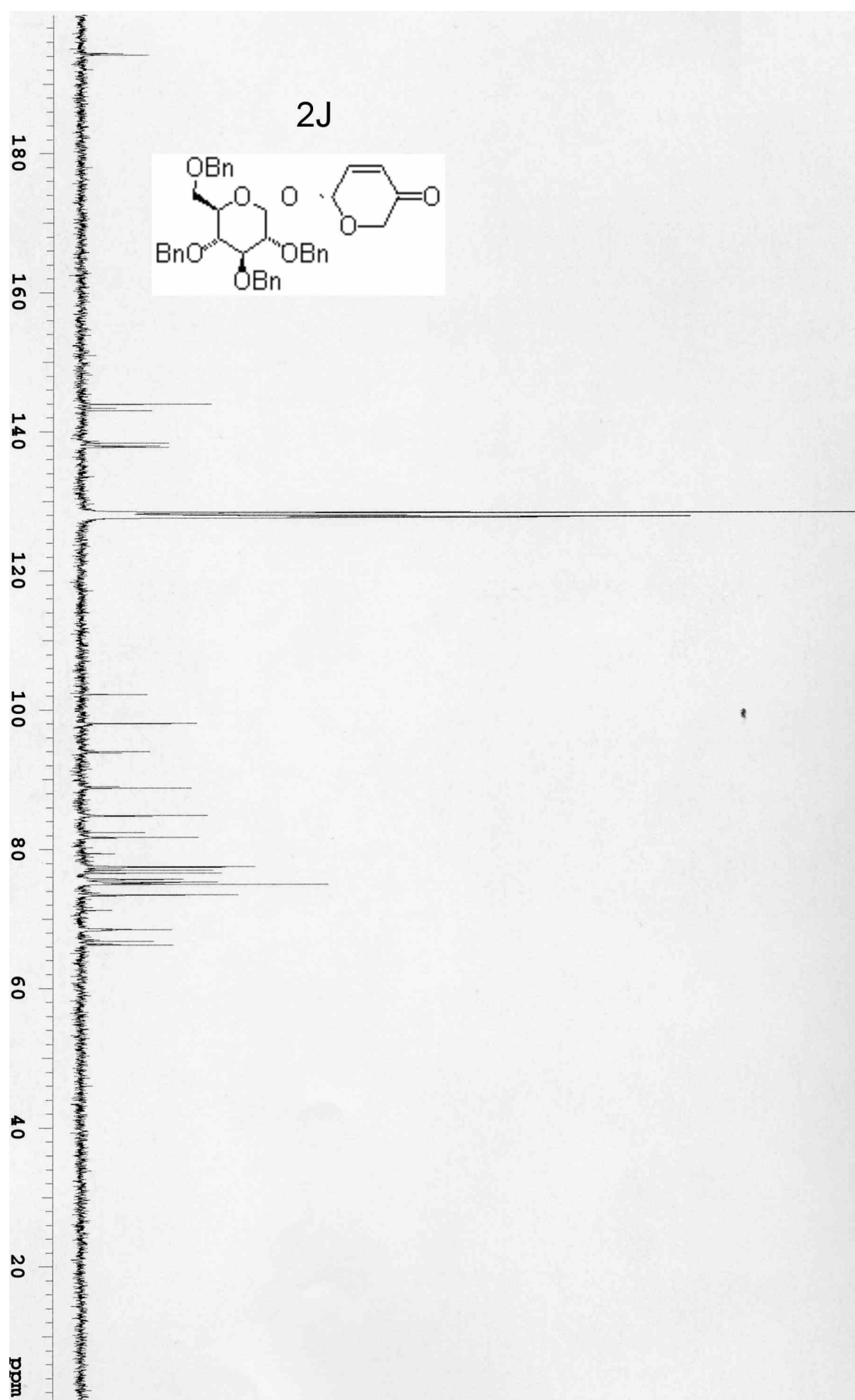


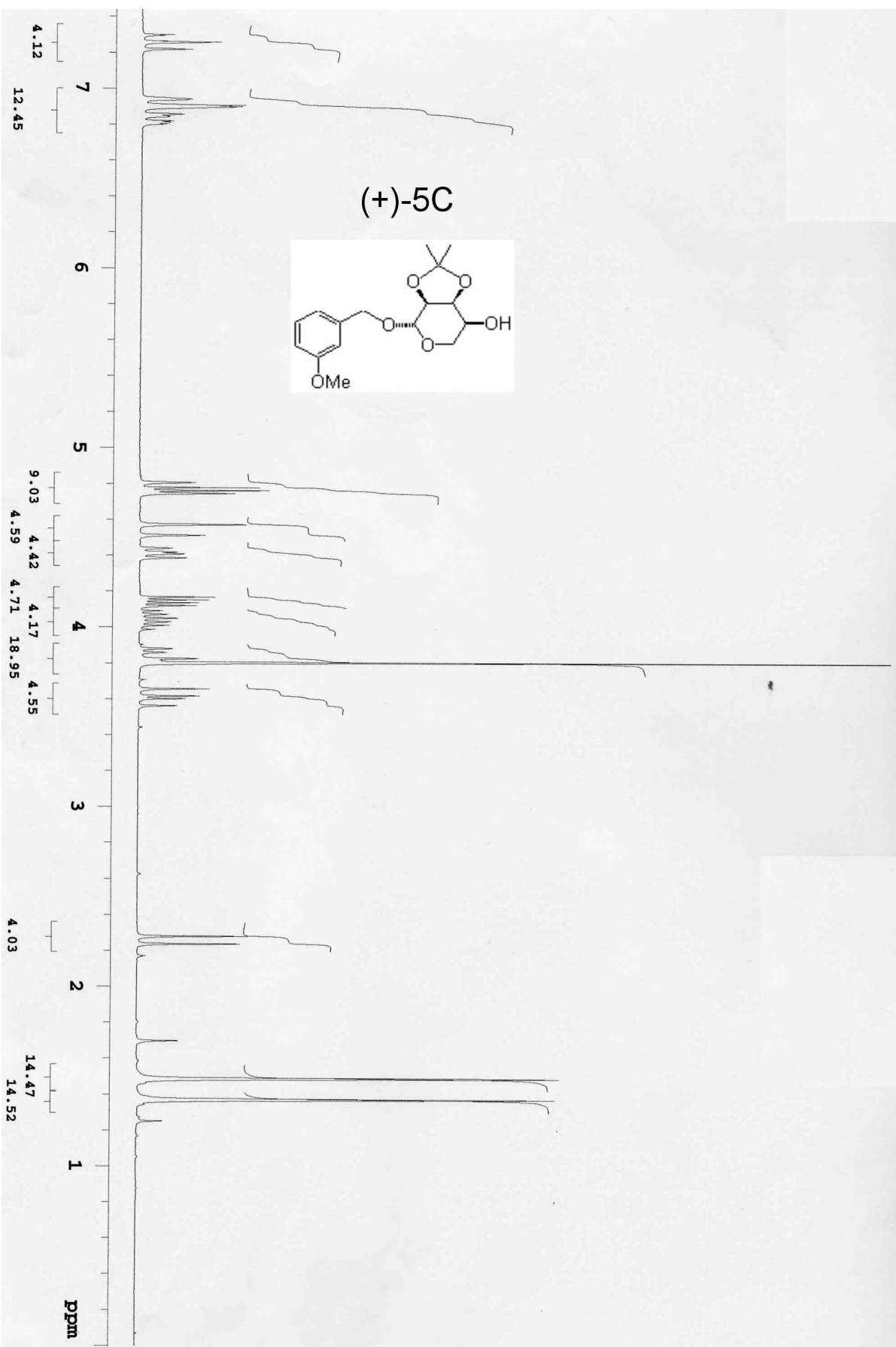
6(S)-2I



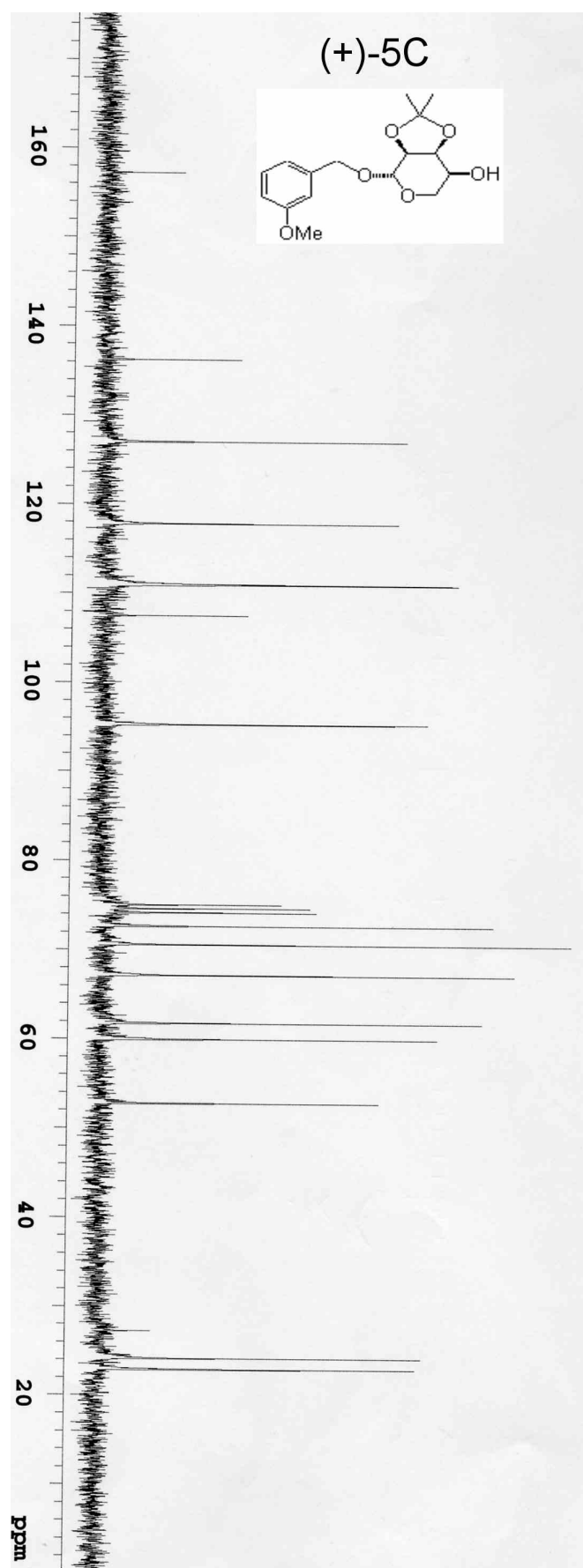
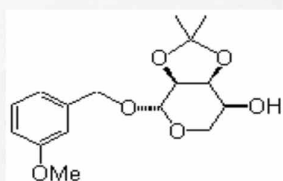
2J

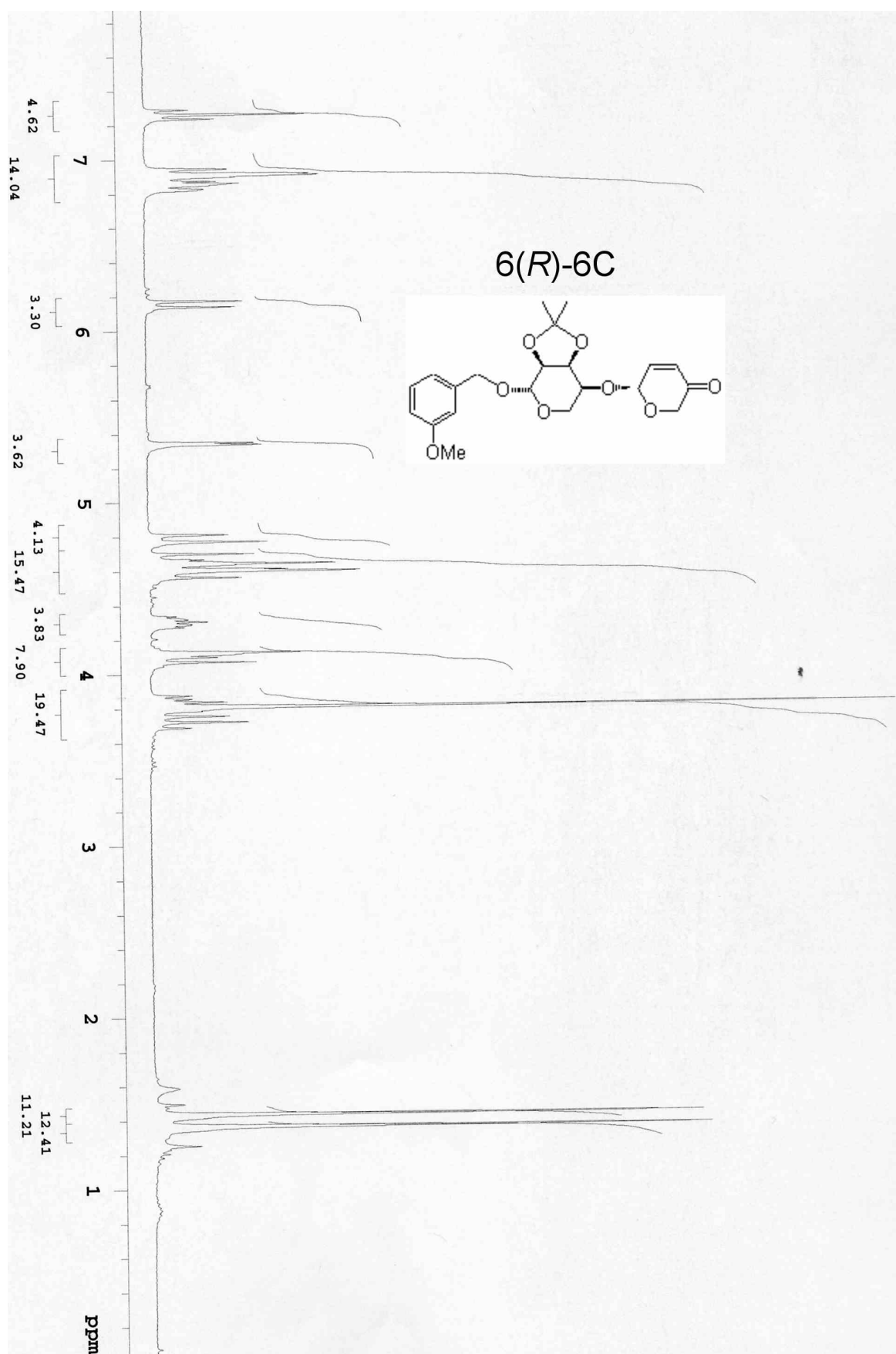




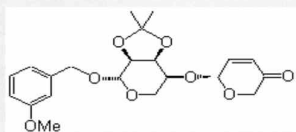


(+)-5C



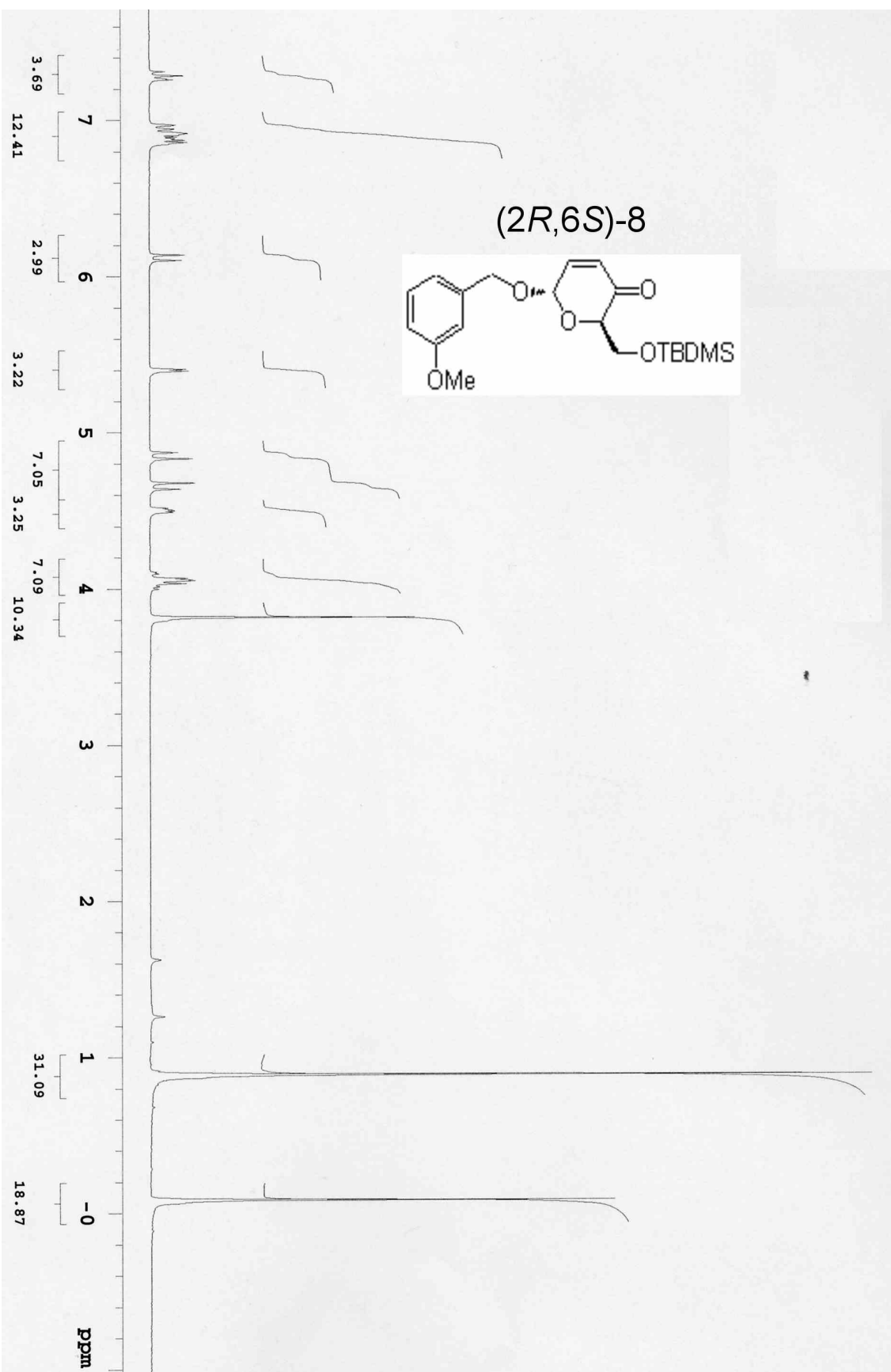
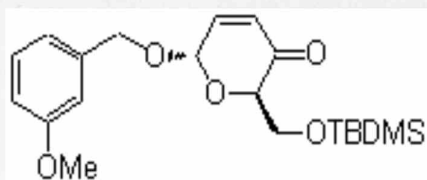


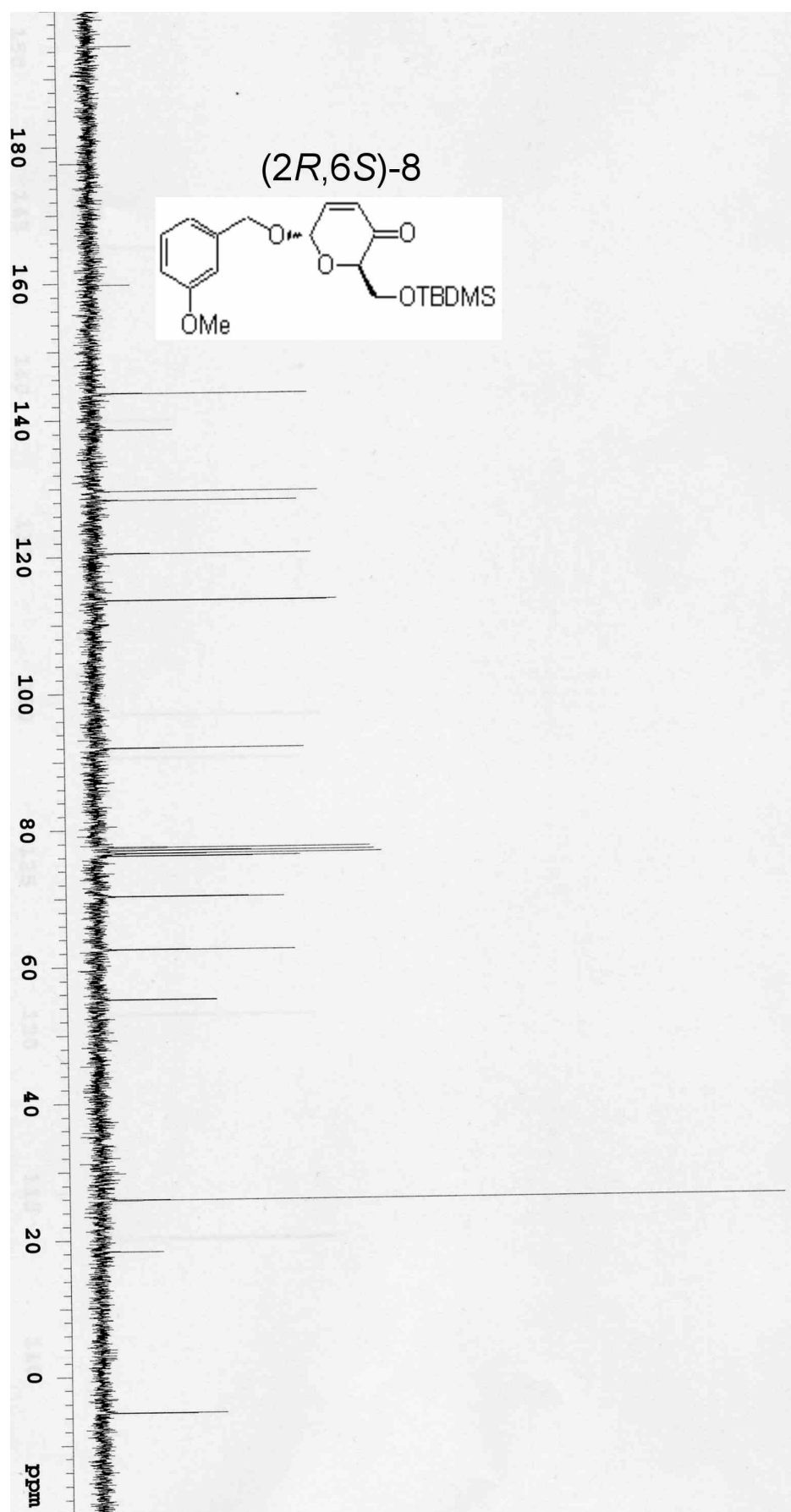
6(*R*)-6C



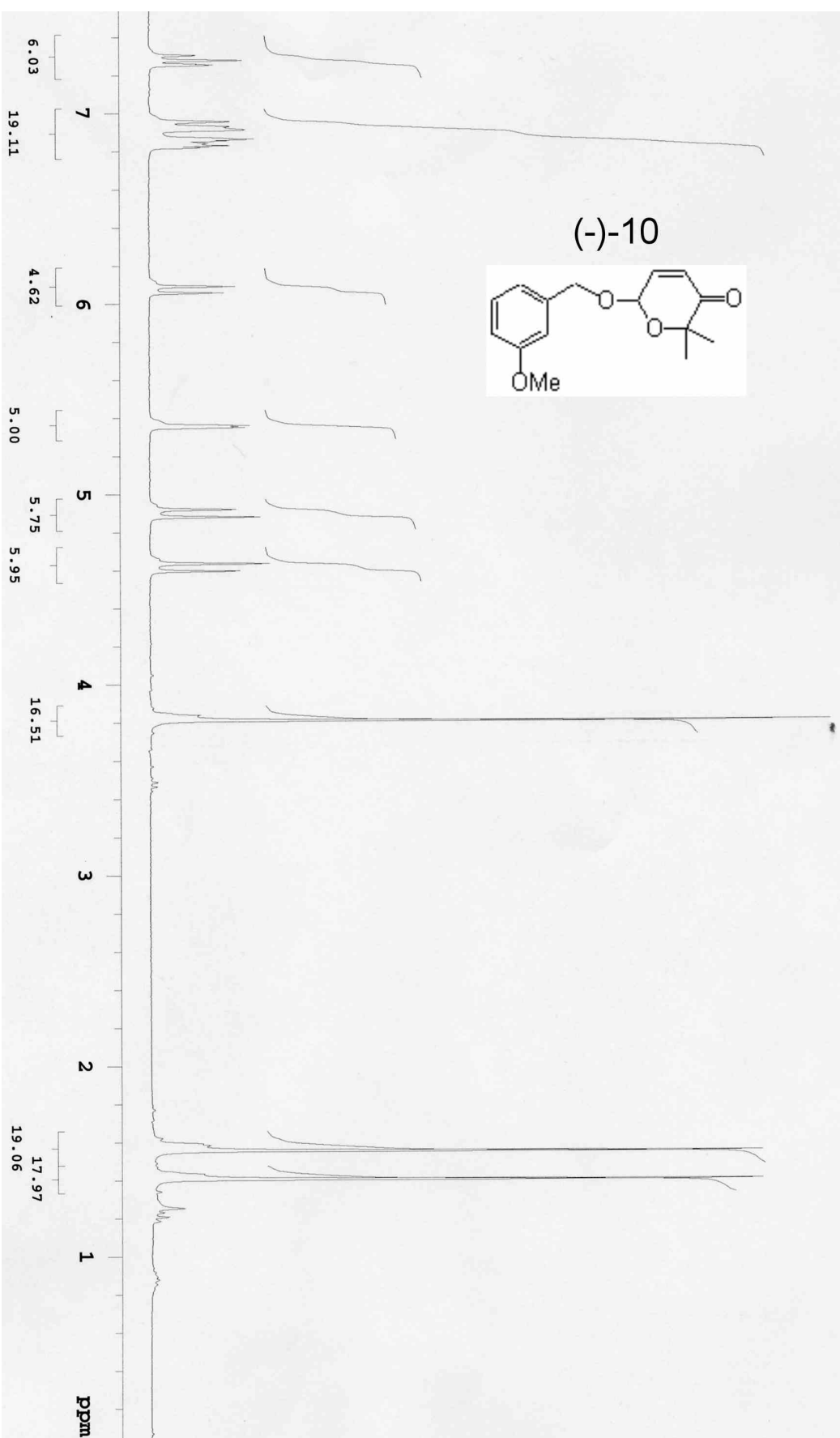
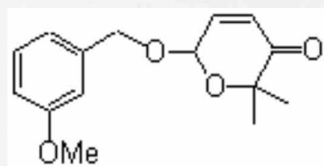
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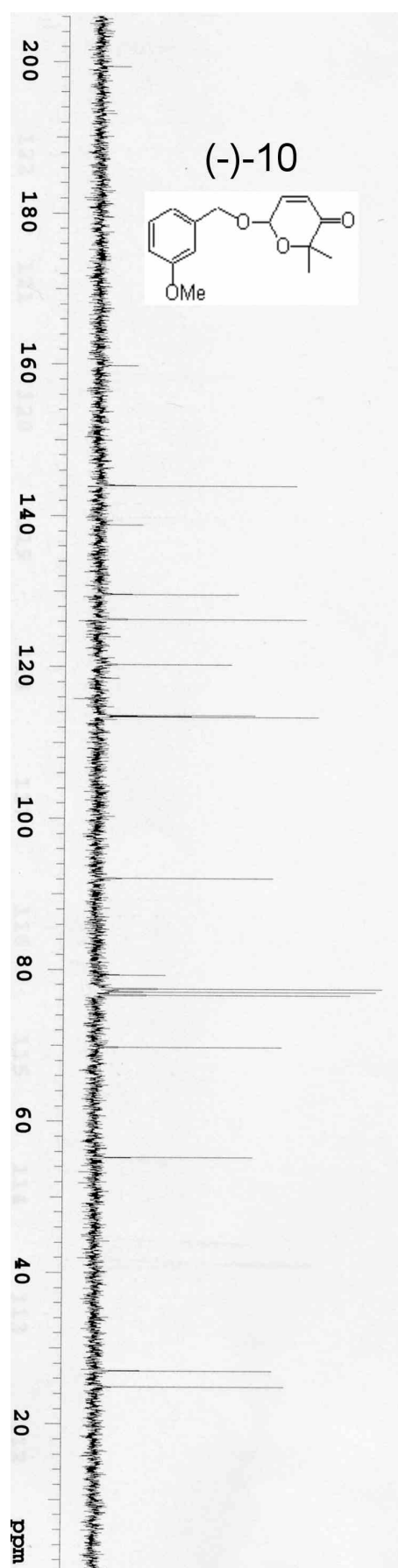
(2*R*,6*S*)-8





(-)-10





41

